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PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY

ERRATA.

VOL. 112 (ABSTR., 1917).

Page. Line.

i. 277 4 *for* "**3:6-dimethyl-1:4-benzopyrone**" *read* "**3:6-dimethyl-2:3-dihydro-1:4-benzopyrone.**"

,, 13 for "3:6-*dimethyl*-1:4-*benzopyrone*" read "3:6-*dimethyl*-2:3-*dihydro*-1:4-*benzopyrone*."

VOL. 117 (TRANS., 1920).

1276 22 *for* "N = 17·37. $C_{13}H_{10}O_6N_4$ requires N = 17·73" *read* "N = 16·35. $C_{20}H_{19}O_6N_5$ requires N = 16·47."

VOL. 118 (ABSTR., 1920)

i. 207 1 *for* "**Potassium**" *read* "**Calcium.**"

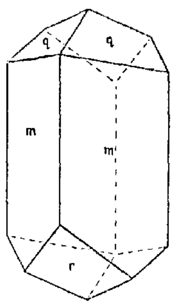
,, 3 ,, "Potassium" ,, "Calcium."

Phenylbenzylmethyl-α-propylammonium Mercuri-iodide, $Ph(CH_2Ph)Et_2NHgI_3$.

—M. p. 134° (Found: Hg = 24·34. $C_{17}H_{22}NI,HgI_2$ requires Hg = 24·36 per cent.). Monoclinic, $a:b:c = 1·1060:1:0·7766$, $\beta = 102°55'$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$, $r\{\bar{1}01\}$, $s\{221\}$, $x\{\bar{2}21\}$. The common habit is shown by Fig. 19. Following are the mean angular values obtained from seven crystals:

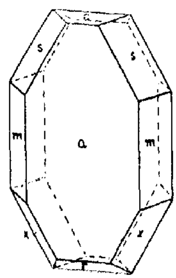
	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$r\{\bar{1}01\}$.	$s\{221\}$.	$x\{\bar{2}21\}$
Azimuth (ϕ)	90° 0′	*42°51′	89°52′	270° 0′	*47° 4′	321°45′
Polar distance (ρ)	90° 0′	90° 0′	12°36′	26°45′	66°19′	63° 1′

FIG. 18.



Phenylbenzyldiethylammonium mercuri-iodide.

FIG. 19.



Phenylbenzylmethylpropyl-ammonium mercuri-iodide.

Cleavage: $a\{100\}$. The optic axial plane is perpendicular to the plane of symmetry, and an optic axis is visible through $m\{110\}$.

Trans.: 100/010/002. Complex-symbol, $(4d;\ +13)64\frac{1}{2}(+2)$.

Our thanks are due to the Research Fund Committee of the Chemical Society and to the Scientific and Industrial Research Department for grants in aid of this work, and also to Professor H. L. Bowman, Mr. J. E. Marsh, and Professor W. H. Perkin for much help and advice.

MINERALOGICAL DEPARTMENT,
UNIVERSITY MUSEUM, OXFORD.

[*Received, September 14th*, 1920.]

CXLII.—*Studies on Hypophosphorous Acid. Part II. Its Reaction with Iodine.*

By Alec Duncan Mitchell.

In estimating hypophosphorous acid by means of mercuric chloride according to the method given by Treadwell ("Quantitative Analysis," p. 289), it was found that the oxidation proceeded readily to phosphorous acid, but relatively slowly to phosphoric acid. It was therefore decided to investigate the progress of the reaction, and certain facts were noted in the first stage—the oxidation to phosphorous acid—which are, briefly:

(1) The concentration of mercuric chloride appeared to have no influence on the reaction velocity except when very dilute.

(2) The reaction was accelerated by the addition of hydrochloric acid.

(3) It was therefore auto-catalytic, owing to the hydrochloric acid produced.

(4) The initial velocity was approximately proportional to the product of the concentrations of the hydrogen ions and the hypophosphorous acid.

From these facts, it was concluded that the oxidation to phosphorous acid involved two successive reactions: the first, of measurable velocity, in which the mercuric chloride took no part, and the second, of relatively great velocity, in which the mercuric chloride functioned. No conventional hypothesis appeared adequately to explain these facts.

In order to investigate certain points more fully, an analogous reaction was sought in which the analytical method used would be of greater applicability. The reaction with iodine was found to be accurately comparable, and is here described. That with mercuric chloride will be communicated later, but it may be mentioned that comparative experiments with iodine and mercuric chloride, respectively, showed that the measurable velocity was identical in the two cases, thus lending additional support to the view that only hypophosphorous acid functions in the slower reaction.

Steele (T., 1907, **91**, 1641) had already investigated the reaction with iodine, and obtained the same general results as above. For the reaction $H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$ he offered the following explanation: the slow stage is represented by

$$(1)\ H_2PO_3' + H_2O \longrightarrow HPO_3'' + 3H^{\cdot} + 2\ominus,$$

which proceeds, liberating free ionic charges, if there is also present a

substance capable of utilising them as rapidly as they are formed: (2) $I_2 + 2\ominus = 2I'$. He points out that several hypothetical schemes may be substituted for (1) in order to account for the production of free electrons, but that intermediate compounds containing iodine cannot be formed in this stage. Any equilibrium between hypophosphorous acid and an "active" form would not agree with the facts if it be assumed that equilibrium is instantaneously restored; but it is now shown that, if equilibrium is restored at a finite rate, the existence of an intermediate "active" form adequately agrees with the facts and renders unnecessary the above unconventional hypothesis.

The reaction has now been studied under more diverse conditions, and certain new aspects have been investigated.

Steele ignored two factors, which are here shown to have an important bearing on the problem:

(1) The depression by mineral acids of the ionisation of hypophosphorous acid, which he regarded as "probably slight." Taking this into account by utilising data obtained in the author's paper on the subject (this vol., p. 957), it is shown clearly that the effect is considerable, and that hypophosphorous acid functions as undissociated molecules. Steele obtained higher constants in stronger acid solutions than in weaker, but, instead of attributing this to the increased proportion of molecules, he ascribed it to the fact that he was using more dilute hypophosphorous acid solutions, the behaviour of which he thought anomalous, and suggested the idea that its ions were the active part of the acid.

(2) The part played by the iodine, which is apparently negligible over small ranges at moderate concentration, but becomes relatively great as the concentration decreases. Steele suggested that it played no part in the reaction until about nine-tenths of it had been used up, but that it then took part in an apparently bimolecular reaction. This is now shown to be erroneous. Also, he was led to ascribe certain discrepancies to the above-mentioned anomalous behaviour of hypophosphorous acid in dilute solution, but these are now shown to be regularised when the function of the iodine is considered.

From the data obtained from about thirty experiments now described, actual rates of decrease (ds/dt) of hypophosphorous acid were calculated at the beginning, middle, and end of each experiment, and when these were divided by the concentrations, at time t, of hypophosphorous acid, l_t, and hydrogen ions, h_t, and by the proportion of undissociated hypophosphorous acid molecules, $1-\alpha_t$, ninety values were obtained for the expression $(ds/dt)/h_t l_t(1-\alpha_t)$ which were almost constant when the corresponding concentrations

of iodine exceeded $N/50$, but which decreased more and more rapidly with decreasing concentrations of iodine. This behaviour was ultimately found to be represented by the formula

$$[1+rh_t/a_t](ds/dt)=kh_tl_t(1-a_t),$$

where a_t represents the concentration of the iodine molecules and r and k are constants.

It will be noticed that this equation takes the form

$$ds/dt=kl_t(1-a_t)h_ta_t/(a_t+rh_t)$$

which the reaction would give if it were simply bimolecular between hypophosphorous acid molecules and iodine, being accelerated by hydrogen ions and retarded by a function, a_t+rh_t, of the iodine. Meyerhoffer (*Zeitsch. physikal. Chem.*, 1888, **2**, 585) found that iodine had a retarding effect, proportional to its concentration plus a constant, on the reaction $HBrO_3+6HI=HBr+3H_2O+3I_2$; but the slightly modified form mentioned above has not been regarded as a valid explanation of the present reaction, since it is difficult to understand why iodine should exert a retarding effect when its concentration is zero, and its acceptance would imply that the hydrogen ions had simultaneously both accelerating and inhibiting effects.

The following hypothesis is found to require the same mathematical expression and to fulfil all the other requirements previously postulated. Hypophosphorous acid molecules are originally in equilibrium with a very small quantity, y, of an "active" form, say H_5PO_3, in which the action of the hydrogen ions is to accelerate re-establishment of equilibrium:

$$H_3PO_2+H_2O \rightleftharpoons H_5PO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the iodine, reacting, as shown later, as the I_3' ion, takes part:

$$H_5PO_3+I_3' \longrightarrow H_3PO_3+2H^{\cdot}+3I' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The rate of formation of phosphorous acid, according to (4), will be:

$$ds/dt = k_2y_ta_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

k_2 being a very large reaction velocity-constant. The equilibrium in (3) is

$$kl_t(1-a_t)h_t=k_1y_th_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

k and k_1 being the reaction velocity-constants in the two directions, k_1 being large, but not infinite, and the amount, y_t, being so small as not appreciably to affect the amount of hypophosphorous acid.

Then the rate of increase in y, owing to the tendency to restore equilibrium, is $kl_t(1-a_t)h_t-k_1y_th_t$, from (6), and its rate of decrease is ds/dt; hence

$$dy/dt=kl_t(1-a_t)h_t-k_1y_th_t-ds/dt \quad . \quad . \quad . \quad . \quad (7)$$

Eliminating y_t from (5) and (7), we have

$$(d^2s/dt^2)/k_2 + (ds/dt)^2/k_2a_t + [a_t + k_1h_t/k_2]ds/dt = ka_tl_t(1-\alpha_t)h_t \quad (8)$$

This expression can be simplified for most reactions, as follows. Since k_2 is very large and k_1 moderately large compared with k, and d^2s/dt^2 and $(ds/dt)^2$ are of a lower order of magnitude than the other terms, and, moreover, are of opposite sign (except in certain cases), the first two terms may be neglected as a first approximation, and one has

$$[a_t + k_1h_t/k_2]ds/dt = ka_tl_t(1-\alpha_t)h_t$$

or

$$[1 + k_1h_t/k_2a_t]ds/dt = kl_t(1-\alpha_t)h_t \quad . \quad . \quad . \quad . \quad (9)$$

which is identical with the formula obtained experimentally when the constant k_1/k_2 is replaced by the constant r. As the best value of r is found to be 0·012, this explains why the iodine appears not to function until it becomes dilute, when a_t is small.

Now, $l_t = l - s$, $a_t = a - s$, and $h_t = h + ms$, since h_t is found to be a linear function of s. If, therefore, α_t is a simple function of s, the expression can be integrated. In some cases it is a linear function, so that $\alpha_t = \alpha - ns$. Letters without suffixes denote initial values, and m and n are constants for any particular experiment. The expression simplifies to

$$k\,.\,dt = ds[1/(l-s)(h+ms)(1-\alpha+ns) + r/(l-s)(a-s)(1-\alpha+ns)] \quad (9a)$$

and one obtains, on integration,

$$kt = \frac{1}{(1-\alpha+nl)(h+ml)[m(1-\alpha)-hn]}\left[\{m(1-\alpha)-hn\}\log\frac{l}{l-s} - n(h+ml)\log\frac{1-\alpha+ns}{1-\alpha} + m(1-\alpha+ln)\log\frac{h+ms}{h}\right] +$$

$$\frac{0{\cdot}012}{(l-a)(1-\alpha+ln)(1-\alpha+na)}\left[(1-\alpha+ln)\log\frac{a}{a-s} - (1-\alpha+na)\log\frac{l}{l-s} + n(l-a)\log\frac{1-\alpha+ns}{1-\alpha}\right] \quad . \quad . \quad (10)$$

In cases where α_t is not sufficiently nearly a linear function of s, it is better to put $n=0$, regarding α as constant, and subsequently to employ the average value of $(1-\alpha)$ for the period concerned in obtaining the value of the constant. Thus one has

$$(1-\alpha)kt = \left[\log l \text{——} l - s + \log\frac{h+ms}{h}\right]\Big/(h+ml) + 0{\cdot}012\left[\log\frac{a}{a-s} - \log\frac{l}{l-s}\right]\Big/(l-a) \quad . \quad . \quad (11)$$

The exceptional cases mentioned when simplifying (8) to (9) are those in which the initial hydrogen-ion concentration is relatively

small and the reaction velocity increases at first to a maximum, so that d^2s/dt^2 is not negative until that maximum is passed. These cases give results in fair agreement with the others when formula (11) is used, so that even when both the neglected terms in (8) are positive, their combined effect is very slight.

It is interesting to note that if hydrogen ions actually took part in the reaction (3) in one direction only, and were not merely catalytic, h_t would disappear from the second term on the left of equation (9), and the theory would require results not consistent with practice.

In the calculations, it is assumed that α for the hypophosphorous acid depends only on the initial amount present and on the concentration of the hydrogen ions, and is not affected by the replacement of hypophosphorous acid by phosphorous acid. This assumption is justified, because the ionising powers of the two acids are very similar, and the total of the two acids remains unchanged, so that, according to the "total ion" hypothesis (Arrhenius, *Zeitsch. physikal. Chem.*, 1888, **2**, 285; 1899, **31**, 218; Bray and Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 781; and Mitchell, this vol., p. 957), for any definite hydrogen-ion concentration there is a definite value of α for each initial concentration of hypophosphorous acid. Also it does not appear that the undissociated molecules of the mineral acids have any appreciable catalytic influence in the concentrations used.

In several experiments (Nos. I, II, and V), possible oxidation to phosphoric acid was checked alkalimetrically (see p. 1332) and found to be negligible. It has, indeed, been shown to be inhibited in an acid medium (Boyer and Bauzil, *J. Pharm. Chim.*, 1918, [vii], **18**, 321), and Federlin (*Zeitsch. physikal. Chem.*, 1902, **41**, 565) could only obtain measurable velocities for the reaction between phosphorous acid and iodine by using concentrated solutions.

In one phase of this work, in order to obtain small yet constant concentrations of hydrogen ions, a "regulator" solution was used, consisting of equimolecular proportions of phosphoric acid and potassium dihydrogen phosphate, so that in the reaction-mixture each was present in molar concentration. Since the concentration of hydrogen ions was constant, the degree of ionisation of hypophosphorous acid was also constant, and, for these experiments, (9) becomes

$$(1+r'/a_t)ds/dt=k'l_t \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where r' and k' are constants, r' being assigned the value 2·0 as giving most consistent results. Attempts to relate r' to rh and k' to $k(1-\alpha)h$, which they replace, are complicated by lack of

sufficient data for such concentrated solutions, but h is of the order $N/50$ and $(1-\alpha)$ about 0·4, so that it is concluded that both k' and r' are several times greater than would be expected.

Owing to the form of equations (11) and (12), in many cases they gave extremely concordant values of a constant based on the equation $ds/dt = k''l_t\sqrt{a_t}$, which was found not to hold when applied to iodine concentrations of a different order. In experiments XI, XX, and XXV this constant is given, as well as k or k', as an interesting example of the danger of relying on what happens to be merely a mathematical coincidence.

The integrated form of (12) is

$$k't = \log\frac{l}{l-s} + \frac{2\cdot 0}{l-a}\left(\log\frac{a}{a-s} - \log\frac{l}{l-s}\right) \quad . \quad . \quad (13)$$

The I_3' *Ion*.—Considering the equilibrium $I_3' \rightleftharpoons I_2 + I'$ investigated by Jakowkin (*Zeitsch. physikal. Chem.*, 1896, **20**, 19), it can be shown that, for any stage of the reaction,

$$[I_2] = K(a-s)/(p+s-a)$$

to a close degree of approximation, where p is the molar concentration of the potassium iodide (assumed completely ionised), and that $[I_3'] = (a-s)[1-K/(p+s-a)]$, since p increases by $2s$ and a decreases by s, when s molecules of iodine have been changed to iodide ions. At the beginning of an experiment, when s is zero, $[I_2] = Ka/(p-a)$, and is therefore independent of the concentration. It was at first thought that this would account for the peculiar behaviour of the iodine in apparently not affecting the velocity of the reaction; but $[I_2]$ decreases more rapidly than $a-s$ with increase of s, so that, if the iodine reacted as such, its apparent active mass should fall off more rapidly than $a-s$, whereas actually it changes far less rapidly. Moreover, a comparison was made in experiments XII and I which were identical, except that in XII potassium iodide was added, so that p was equal to $9\cdot 78a$, whereas in I it was $3\cdot 76a$; if molecular iodine were the active factor, the initial reaction velocities should be in the ratio 2·76 to 8·78, whereas they were almost identical. Experiments XXV and XXVI also illustrate this in presence of the "regulator" solution. The iodine therefore does not react as molecules.

Thus it is the I_3' ion which functions, and, using the constant 0·00135 given by Jakowkin for the equilibrium, it is found that this ion constitutes 99 per cent. of the available iodine in $N/10$-solutions, but is less in weaker solutions, being only about 65 per cent. in $N/400$-solutions at the beginning of reactions, and increasing somewhat as the reaction proceeds. This change in the relative concentration of the I_3' ion has been ignored throughout, as the

correction involved only affects the smaller term, and is, moreover, less at the end of a reaction than at the beginning, since the increase of iodide ions outweighs the effect of dilution, and thus increases the proportion of I_3' ions. It would unnecessarily complicate equations, which are evidently sufficiently accurate to demonstrate the validity of the hypothesis.

In conclusion, it may be said that, whatever the nature of the supposed "active" form of hypophosphorous acid, its existence could probably not be detected by chemical means, and, as the indications are that it is less than 1 per cent. of (and in constant proportion to) the acid molecules, its detection by physical means would be difficult. It is also possible that another hypothesis could be found which would require similar mathematical expression, but, if so, it is certainly more complicated than that developed here.

Experimental.

The reactions were carried out in stoppered brown glass bottles in a thermostat at $25 \pm 0{\cdot}05°$. The iodine solution and hydrochloric acid or "regulator" solutions, when used, were made up to 400 c.c., and when they had acquired the temperature of the thermostat, 1·013, 2·000, or 4·000 c.c. of a concentrated solution of hypophosphorous acid were added from standardised pipettes. At definite times, quantities were withdrawn and run into a large volume of water containing the volume of standard sodium thiosulphate solution estimated to be necessary, and the final adjustment made at once. Check experiments showed that the hypophosphorous acid did not affect the titrations.

The stock iodine solution was accurately decinormal. As it was subsequently required to know the potassium iodide content of this solution, it was found to be 31·2 grams per litre (or 3·76 molecules per molecule of iodine) by an adaptation of the method with potassium iodate described by Sutton ("Volumetric Analysis," p. 133).

The stock hypophosphorous acid solution was a chemically pure article of commerce (D 1·14) which showed no impurities other than a little phosphorous acid. Its composition was checked by two methods: 25 c.c. of a one-tenth solution gave 1·5124 grams of $Mg_2P_2O_7$, therefore $H_3PO_2 + H_3PO_3 = 5{\cdot}45$ moles. per litre; 20 c.c. of one-fiftieth solution required 21·80 c.c. of $N/10$-NaOH with methyl-orange, and 22·60 c.c. with phenolphthalein. Since hypophosphorous acid is monobasic to both indicators and phosphorous acid is monobasic to the former and dibasic to the latter, the former is 5·25 molar and the latter is 0·20 molar, thus giving

a total identical with the gravimetric value. For obtaining the value of l, the solution was regarded as $5 \cdot 25N$, and the values of the hydrogen ions were based on a normality of 5·45, since the second hydrogen ion of phosphorous acid can be ignored.

Calculation of Results.—The degrees of dissociation of hydrochloric acid are taken from the results of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781), and the hydriodic acid is reckoned as hydrochloric acid for this purpose. The degree of dissociation of the hypophosphorous acid in the presence of the mineral acids is obtained by methods based on the author's recent communication on the subject (this vol., p. 957). From table I given therein, a curve is constructed showing the relation between α and the concentration of hydrogen ions, α/v, when no extraneous acid is present. From this it is possible to obtain a series of curves, one for each value of l, showing the relation between α and the concentration of extraneous hydrogen ions ($H^{\cdot}_{x}$), as follows: for a definite concentration of hypophosphorous acid, l, the value of α when $H^{\cdot}_{x}$ is zero can be obtained at once. A slightly lower value, α_1, is then selected, and the concentration of hydrogen ions in equilibrium with the acid alone at that degree of ionisation is found from the first curve; this must also be the concentration of hydrogen ions in the equilibrium if foreign acid is present, as shown in the paper quoted; from this is therefore deducted $l\alpha_1$, due to the hypophosphorous acid itself, and the remainder is $H^{\cdot}_{x}$. A series of corresponding values of α and $H^{\cdot}_{x}$ is obtained in this way for each value of l, and from the resulting curve the value of α can be obtained for a known $H^{\cdot}_{x}$. This method is simpler and of wider applicability than solving the equation developed in the former communication.

In order to avoid small decimals, all concentrations are multiplied by 200, and the value of k should therefore be multiplied by 200 in order to give absolute units. Time, t, is in minutes; $a-s$ shows the iodine concentration in molecules; s shows the number of moles. reduced; $l-s$ the hypophosphorous acid remaining. The column HI shows the original hydrochloric acid (when used) plus $2s$, the hydriodic acid formed. $H^{\cdot}_{HI}$ are the corresponding hydrogen-ion concentrations of the mineral acids, the degree of ionisation (not recorded) being assumed to be unaffected by the presence of the weaker acids. α gives the degree of dissociation of the hypophosphorous and phosphorous acid, and under $H^{\cdot}_{P}$ is recorded $l\alpha$, the hydrogen ions derived from them, the slight correction necessary for the phosphorous acid initially present having been made throughout. Then follow the total hydrogen-ion concentration, h, and $1-\alpha_M$, the mean value of $1-\alpha$ for the period

(or $1-\alpha_{M}$, the value at the middle of the period), for which the constant k is calculated.

Formula (11) is used except where otherwise stated, and in any one experiment the deviations of k from the mean rarely exceed 3 per cent.

The six following experiments were without original hydrochloric acid.

Experiment I.

t.	$a-s$.	s.	$l-s$.	HI.	$H^{\cdot}_{HI}$.	a.	$H^{\cdot}_{P}$.	h.	$1-a_{M}$.	$k\times10^5$
0	4·99	—	10·52	—	—	0·645	7·10	7·10	—	—
5	4·82	0·17	10·35	0·34	0·34	0·640	6·99	7·33	0·355	118
20	4·34	0·65	9·86	1·31	1·28	0·625	6·77	8·05	0·365	114
50	3·29	1·70	8·82	3·40	3·27	0·590	6·44	9·71	0·382	112
80	1·96	3·03	7·48	6·07	5·77	0·553	6·00	11·77	0·400	117
105	0·98	4·01	6·51	8·02	7·58	0·530	5·79	13·37	0·413	118
125	0·19	4·80	5·72	9·59	9·02	0·513	5·58	14·60	0·421	120
145	0·03	4·96	5·56	9·93	9·34	0·510	5·57	14·91	0·422	113

$m = 1·543$. Mean = 116

The data of the other five experiments gave constants of the same order of agreement, and are here summarised.

Expt.	a.	l.	a.	$H^{\cdot}_{P}=h$.	m.	$k\times10^5$.
II.	9·80	20·62	0·552	11·81	1·546	148
IV.	9·92	5·34	0·735	4·07	1·651	134
V.	9·86	10·44	0·645	7·05	1·606	124
VI.	2·43	25·50	0·525	13·91	1·425	139
VII.	2·46	13·00	0·622	8·40	1·507	120

[In experiment VII, the complete formula (10) was used with $n=0·030$.]

The following experiment is comparable with I, and shows the negligible effect of adding more potassium iodide (see p. 1327):

XII.	4·97	10·44	0·650	7·05	1·566	114

The next thirteen experiments were with initial hydrochloric acid. Only experiments III and XVI are given in detail, the latter showing the accuracy of the constant at very low concentrations of iodine.

Experiment III.

t.	$a-s$.	s.	$l-s$.	HI.	$H^{\cdot}_{HI}$.	a.	$H^{\cdot}_{P}$.	h.	$1-a_{M}$.	$k\times10^5$.
0	4·93	—	10·44	11·30	10·59	0·496	5·38	15·97	—	—
5	4·33	0·60	9·84	12·51	11·68	0·485	5·26	16·94	0·510	(139)
10	3·89	1·04	9·40	13·38	12·47	0·478	5·18	17·65	0·513	126
15	3·34	1·59	8·85	14·48	13·47	0·470	5·10	18·57	0·517	129
20	2·80	2·13	8·31	15·56	14·44	0·463	5·02	19·46	0·520	130
25	2·31	2·62	7·82	16·55	15·35	0·457	4·95	20·30	0·524	129
30	1·81	3·12	7·32	17·55	16·24	0·450	4·88	21·12	0·527	130
35	1·40	3·53	6·91	18·37	16·97	0·445	4·82	21·79	0·530	127
40	0·95	3·98	6·46	19·25	17·75	0·439	4·76	22·51	0·533	128
45	0·57	4·36	6·08	20·02	18·44	0·434	4·70	23·14	0·535	128
50	0·28	4·65	5·79	20·60	18·95	0·430	4·66	23·58	0·537	128
55	0·11	4·82	5·62	20·94	19·26	0·428	4·64	23·90	0·538	128
60	0·04	4·91	5·53	21·12	19·41	0·426	4·62	24·03	0·539	130

$m = 1·644$. Mean = 128

Experiment XVI.

t.	$a - s$.	s.	$l - s$.	HI.	$H^{\cdot}_{HI}$.	a.	$H^{\cdot}_{P}$.	h.	$1 - \alpha_M$.	$k \times 10^5$
0	0·499	—	2·670	14·10	13·13	0·515	1·43	14·56	—	—
2	0·460	0·039	2·631	14·18	13·20	—	1·42	14·62	0·486	(135)
7	0·389	0·110	2·560	14·32	13·33	—	1·42	14·75	—	116
12	0·319	0·180	2·490	14·46	13·47	—	1·42	14·89	—	116
16	0·267	0·232	2·438	14·57	13·56	—	1·41	14·97	—	116
22	0·196	0·303	2·367	14·71	13·68	—	1·40	15·08	—	116
28	0·141	0·358	2·312	14·82	13·79	—	1·40	15·19	—	116
44	0·043	0·456	2·214	15·01	13·96	0·503	1·39	15·35	0·491	116

$m = 1·73$. Mean = 116

Expt.	a.	l.	HI.	$H^{\cdot}_{HI}$.	α.	$H^{\cdot}_{P}$.	m.	$k \times 10^5$.
XIV.	9·76	10·30	11·10	10·41	0·498	5·33	1·647	128
XV.	0·250	2·670	28·20	25·66	0·409	1·13	1·830	136
XVII.	0·250	2·670	14·10	13·13	0·515	1·43	1·764	132
XVIII.	0·986	1·040	28·0	25·5	0·415	0·45	1·66	123
XIX.	9·58	20·20	10·86	10·19	0·459	9·64	1·572	145
XX.	0·985	2·080	28·0	25·5	0·412	0·9	—	122
XXI.	0·985	2·080	11·20	10·47	0·550	1·20	1·81	112
XXII.	0·493	1·040	28·0	25·5	0·415	0·44	—	137
VIII.	4·97	2·67	113·0	96·0	0·25	—	—	137
IX.	2·485	2·67	56·5	51·0	0·30	—	—	129
XI.	2·485	2·67	113·0	96·0	0·25	—	—	131

Where no value is given for m, h is regarded as constant, and in the last three experiments the value of $H^{\cdot}_{P}$ has been neglected, as not appreciably affecting the total value of h. Also, in the last three experiments, a was obtained by extrapolation, and is therefore only approximate.

In experiment XI, eight values, all between 300 and 312, were obtained for the constant $k'' \times 10^4$ mentioned on p. 1327. In experiment XX, similarly all ten values were between 107 and 112.

The following seven experiments were in a solution molar with respect to both phosphoric acid and potassium dihydrogen phosphate as "regulator" (see p. 1326). Formula (13) is used in each case. Experiment XXIII is given in detail.

Experiment XXIII.

t.	$a - s$.	s.	$l - s$.	$k' \times 10^4$.
0	4·996	—	10·50	—
2	4·596	0·400	10·10	274
6	3·898	1·098	9·40	267
10·2	3·246	1·750	8·75	268
15	2·578	2·418	8·08	272
20	1·996	3·000	7·50	274
25	1·522	3·474	7·03	274
33	0·950	4·046	6·40	276
45	0·432	4·564	5·94	276

Mean 272

Expt.	a.	l.	$k' \times 10^4$.
XXIV.	4·970	5·224	271
XXV.	2·494	5·250	254
XXXI.	0·4992	1·050	264
XXXII.	0·2496	1·050	291
XXXIII.	0·4992	0·525	266
XXXIV.	0·4994	5·250	240

For XXV, all eight values of $k'' \times 10^4$ (p. 1327) are between 600 and 626.

Experiment XXVI was exactly comparable with XXV, except that it contained potassium iodide in the proportion of 15·8 molecules to each molecule of iodine; XXV, and all other experiments except XII, have the proportion 3·76. The constant, $k' \times 10^4$, was 255; the agreement with 254, obtained in XXV, shows that iodine functions as the I_3' ion.

Experiment XXVII, at 11·6°, gave a constant, $k' \times 10^4 = 54·8$, and as it is exactly parallel with XXV, the temperature-coefficient is 4·64 for 13·4 degrees. Logarithmic proportion reduces this to 3·14 for 10 degrees and 2·22 for 7 degrees. Steele found 3·1 for 10 degrees for solutions without added acid or "regulator." Since the term involving r', the ratio between two rapid reaction velocities (see formula 12), accounts for more than half the value of the constants, it appears that this ratio is practically unaltered over the range of temperature employed.

The agreement between the constants obtained in this series of "regulator" experiments shows clearly that the iodine must function in the manner shown in the equations used. The effect of neglecting it is very much more apparent in this series than in the earlier experiments.

In order to detect possible oxidation to phosphoric acid, the following procedure was adopted. If phosphorous acid only is produced, each molecule of iodine reduced gives rise to 2 molecules of hydriodic acid, and also changes 1 molecule of monobasic hypophosphorous acid to 1 molecule of dibasic phosphorous acid, phenolphthalein being used as indicator; whereas, if phosphoric acid is produced, 2 molecules of iodine give rise to 4 molecules of hydriodic acid, and still only raise the basicity by unity. Therefore, in the former case, the increase of acidity should be 1·5 times the number of equivalents of iodine consumed, and in the latter case the ratio should be 1·25. In every case tested, the ratio has been very close to 1·5, so that the production of phosphoric acid is very slight.

Expt. I.—At t_{145}, 20 c.c. required 14·84 c.c. of $N/10$-NaOH more than at t_0; iodine consumed = 9·93 c.c. of $N/10$-$Na_2S_2O_3$; ratio = 1·495.

Expt. II.—Increase of alkali titre at $t_{50}=14·63$ c.c.; iodine consumed $=9·75$ c.c.; ratio $=1·501$.

Expt. V.—Increase of alkali titre at $t_{150}=19·58$ c.c.; iodine consumed $=13·10$ c.c.; ratio $=1·495$.

For the same purpose in the "regulator" series, an experiment (XXVIII) was carried out exactly parallel with XXV, except that hypophosphorous acid was replaced by the same concentration of phosphorous acid. In three hours, less than one-half per cent. of the iodine was reduced, whereas in experiment XXV, 50 per cent. was reduced in twenty-two minutes.

Experiment X was carried out with hypophosphorous acid which was previously neutralised (to methyl-orange), and is comparable with I. In five hours, less than 5 per cent. of the iodine was reduced; as the second hydrogen ion of the phosphorous acid, originally present to a slight extent, would be sufficient to start the reaction, and so provide more hydrogen ions, it is probable that reaction in neutral solution is extremely slow, and that the H_2PO_2' ion does not react, except, possibly, in the presence of hydrogen ions, in which case reaction is evidently so slow as not greatly to affect the constancy of values obtained on the assumption that it does not take place at all.

The following experiments of Steele's are quoted, after conversion to the units used herein, to show how the irregularities observed by him are largely accounted for in the light of the present work. The first two columns are derived from his data; the remainder are obtained as in the author's results. The constants obtained by each method are shown, those of Steele being designated by K_S. The letter S after the Roman numerals indicates his experiments.

The value 119 obtained for $k \times 10^5$ in X(S) is in agreement with the author's results, and shows less falling off with time than does K_S. Moreover, for the three experiments, the results are far more concordant than those obtained on Steele's hypothesis. The fact that Steele used a very pure specimen of hypophosphorous acid may account for the slightly lower values in his experiments.

Expt.	a.	l.	α.	$H^{\cdot}_P = h$.	$k \times 10^5$.	$K_S \times 10^3$.
X(S)	2·00	20·00	0·555	11·10	119	94
XI(S)	0·500	5·00	0·734	3·67	92	45
XII(S)	0·200	2·00	0·841	1·68	83	24·5

Although the agreement is not so good as in the other results, it is evidently far better than in the results obtained by Steele's method, so that the present hypothesis, which attributes a definite part to the iodine molecules, is apparently more justified by results than that which ignores the iodine and attributes the great decrease

in the constant to a decreased activity of hypophosphorous acid at low concentrations.

This is further supported by a reconsideration of Steele's experiment II, for which he could not obtain a constant without assuming the degree of ionisation to be 0·20 instead of the actual 0·775, which was again supposed to be due to decreased activity. According to the present method, one obtains moderate constancy.

Experiment II(S) at 18°.

t.	$a-s$.	s.	$l-s$.	$H^{\cdot}_{III}$.	a.	$H^{\cdot}_{P}$.	h.	$1-a_H$.	$k \times 10^5$.
0	4·50	—	4·00	—	0·775	3·11	3·11	—	—
390	4·20	0·30	3·70	0·60	0·750	3·00	3·60	0·235	(25·3)
570	3·98	0·52	3·48	1·02	0·735	2·94	3·96	0·245	(28·1)
1440	2·42	2·08	1·92	4·00	0·660	2·64	6·64	0·280	38·3
1710	2·04	2·46	1·54	4·68	0·643	2·56	7·24	0·290	37·7
1830	1·84	2·66	1·34	5·04	0·636	2·54	7·58	0·295	39·2
2805	0·80	3·70	0·30	6·96	0·597	2·38	9·34	0·340	41·5
3240	0·68	3·82	0·18	7·24	0·592	2·36	9·60	0·355	39·8

m — 1·675. Mean = 39·3

If the temperature-coefficient for seven degrees is taken as 2·22 (see p. 1332), this gives the low value of 87 for 25°, but, that the experiments correspond in general is seen from the following summary of experiments, for which the data can be utilised:

Experiment.	III(S).	IV(S).	V(S).	VIII(S).	XIII(S).	XV(S).	XXI(S)
$k \times 10^5$	108	115	119	105	107	113	119
$K_S \times 10^4$	355	400	425	430	425	505	555

Steele's $K_S \times 10^4$, given for comparison, clearly shows the inadequacy of his hypothesis.

The method of treatment now presented obviously places the question on a more systematic basis, although the slight variation of the "constant" from one experiment to another is not accounted for; but the several small approximations made, together with the uncertainty in the choice of the value of the constant r, the large influence, in certain cases, of a difference, $l-a$, which is sometimes very small, and the alteration in the proportion of the iodine which is present as the I_3' ion, may easily account for the variation of 10 per cent. from the mean value, 128×10^{-5}. It is also probable that the H_2PO_2' ions react slowly, and account partly for the variations, since the three highest constants are given by the three greatest concentrations of hypophosphorous acid.

Summary.

(1) The previous attempt to explain the reaction had suggested an hypothesis involving the presence of free ionic charges. By taking

into consideration certain factors which had been ignored, this is shown to be unnecessary, and most discrepancies disappear.

(2) These factors were: (i) the influence of the iodine concentration on the measurable velocity, this influence being slight at moderate dilution, but relatively large at greater dilution, and (ii) the effect of hydrochloric and hydriodic acids on the ionisation of hypophosphorous acid.

(3) The following hypothesis is advanced to explain all the anomalies formerly noted. The hypophosphorous acid *molecules* are in equilibrium with a very small proportion of an "active" form (say H_5PO_3), which reacts rapidly with the iodine,

$$H_5PO_3 + I_3' \longrightarrow H_3PO_3 + 2H^{\cdot} + 3I'.$$

The restoration of the equilibrium thus displaced is accelerated by hydrogen ions, and forms the measurable reaction,

$$H_3PO_2 + H_2O \rightleftharpoons H_5PO_3.$$

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CXLIII.—*Modification and Extension of the Friedel and Crafts' Reaction. Part I.*

By JNANENDRA NATH RÂY.

RADZIEWANOWSKI (*Ber.*, 1895, **28**, 1139) suggested some modifications of the Friedel-Crafts' reaction, in one of which he used a mixture of aluminium powder and mercuric chloride. He prepared ethylbenzene in small yield, but did not obtain any triphenylmethane in the condensation of chloroform and benzene. Von Gulewitsch (*Ber.*, 1904, **37**, 1560) studied the interaction of mercuric chloride and aluminium in benzene, and isolated a compound, $C_6H_6,AlCl_3,HgCl$. A similar compound was formed with toluene. It was thought that if this double compound were employed as a catalyst, the secondary changes that rendered Radziewanowski's reaction unsuccessful might disappear. This expectation has been amply realised. Von Gulewitsch showed the course of the reaction to be

$$C_6H_6 + Al + 2HgCl_2 \longrightarrow C_6H_6,AlCl_3,HgCl + Hg.$$

The mercury, liberated as above, forms an amalgam with the unchanged aluminium, but when an excess of mercuric chloride is employed, this tendency to amalgamate is reduced, inasmuch as

the whole of the aluminium is utilised in reducing mercuric to mercurous chloride. The success of the reaction depends on the non-formation of the amalgam, as otherwise it acts concurrently with the double compound.

Some interesting products have been isolated in the condensation of the hydrocarbons with chloroform, carbon tetrachloride, benzylidene chloride, etc. Thianthren has been prepared in an 80 per cent. yield from benzene and sulphur. This compound was obtained in small amount along with phenyl mercaptan, phenyl sulphide, and phenyl disulphide by Friedel and Crafts (*Ann. Chim. Phys.*, 1888, [vi], **14**, 438) in the condensation of benzene and sulphur with aluminium chloride, whilst Genvresse (*Bull. Soc. chim.*, 1897, [iii], **17**, 599) observed the formation of thianthren and *iso*thianthren in the same reaction.

9:10-Diphenyl-9:10-dihydroanthracene is formed by the condensation of benzene and chloroform, whilst in the ordinary Friedel-Crafts' reaction (*Annalen*, 1878, **194**, 254; 1885, **227**, 107), triphenylmethane, chloroarylmethanes, and tetraphenylethane (*Ber.*, 1893, **26**, 1952) are the products. The same compound is obtained by the interaction of benzylidene chloride and benzene.

Carbon tetrachloride and benzene give 9:9:10:10-*tetraphenyl-9:10-dihydroanthracene*, which is also obtained from benzotrichloride and benzene, whilst in the usual reaction, triphenylmethane, chloroarylmethanes (*Annalen*, 1878, **194**, 254), and tetraphenylethylene (*Ber.*, 1893, **26**, 1952) are obtained.

Similarly, *dimethyl-9 : 10-ditolyl-9 : 10-dihydroanthracene* has been obtained from chloroform and toluene. In this condensation, using aluminium chloride, Schwarz (*Ber.*, 1881, **14**, 1530) prepared tetratolylethane, which has the same melting point (215°) and empirical formula, but a mixture of the two melts at 206—208°. Benzylidene chloride and toluene yield *dimethyl-9:10-diphenyl-9:10-dihydroanthracene*.

Finally, chloropicrin and benzene, under the action of the reagent, furnish ω-nitrotriphenylmethane, previously obtained by the direct addition of nitrogen peroxide to triphenylmethyl (Schlenk, Mair, and Bornhardt, *Ber.*, 1911, **44**, 1172). Boedtker (*Bull. Soc. chim.*, 1908, [iv], **3**, 726) states, however, that all aliphatic nitro-compounds lose their nitro-groups under the influence of aluminium chloride, and obtained triphenylmethane and some triphenylcarbinol in this reaction.

EXPERIMENTAL.

To a mixture of 20 c.c. of dry benzene and 20 grams of mercuric chloride contained in a flask with reflux condenser, 1 gram of aluminium powder was added gradually, and the flask vigorously shaken. The heat of the reaction caused the benzene to boil, and the flask was occasionally cooled in an ice-bath. A green, crystalline mass eventually separated, and the reaction was completed by immersing the flask in tepid water for half an hour. The mercury liberated in the reaction was removed, and the preparation of the catalyst was complete.

In all the reactions described below, the components were well agitated by a mechanical stirrer.

Acetophenone.—The calculated amount (1 mol.) of acetyl chloride was added through the condenser in small quantities at a time, the mixture allowed to remain for two hours at the ordinary temperature, and then heated to 40° for an hour. On cooling, it was decomposed with water, and the oil extracted with benzene, the benzene solution being dried and finally fractionated. The yield of acetophenone was 60 per cent. of the theoretical, whilst by Friedel and Crafts' method it is 55·5 per cent.

p-*Tolyl Methyl Ketone.*—Following an almost identical method, from 33 c.c. of toluene, 2·5 grams of aluminium, and 45 grams of mercuric chloride, 16·1 grams of this ketone were obtained.

Thianthren, $C_6H_4{<}^{S}_{S}{>}C_6H_4$.—The catalyst was prepared from 2·5 grams of aluminium, 45 grams of mercuric chloride, and 30 c.c. of benzene; 10 grams of flowers of sulphur were added, and the mixture was heated on the water-bath until hydrogen sulphide was no longer evolved. The product, on cooling, was decomposed with ice, filtered, and the residue repeatedly extracted with chloroform, from which the substance was obtained on concentration. When crystallised from acetone, it melted at 160°. The yield was 14 grams (Found: C=66·1; H=3·8; S=28·5. Calc.: C=66·6; H=3·7; S=29·6 per cent.).

9:10-*Diphenyl*-9:10-*dihydroanthracene.*—The catalyst was prepared from 1 gram of aluminium, 20 grams of mercuric chloride, and 15 c.c. of benzene. Six c.c. of chloroform were added drop by drop through the condenser, and the flask was allowed to remain at the ordinary temperature for two hours, and then heated for an hour at 40°, and then for another hour at 40—50°. On cooling, the product was decomposed with ice and filtered. There separated from the filtrate a deep red oil, from which some unchanged benzene was evaporated. The residue was extracted with

boiling acetic acid containing a little water, from which the compound separated on cooling. After being crystallised from dilute alcohol, and then repeatedly from dilute acetone, the compound melted at 159° (Linebarger, *Amer. Chem. J.*, 1891, **13**, 556, gives 164·2°) (Found: C=93·2; H=6·7. Calc.: C=93·9; H=6·1 per cent.).

The same compound was obtained by the interaction of 3 c.c. of benzylidene chloride, 8 c.c. of benzene, 0·5 gram of aluminium, and 10 grams of mercuric chloride, the reaction being completed at 50—55°. The product was isolated as described above (Found: C=94·0; H=6·39. Calc.: C=93·9; H=6·1 per cent.). A solution of 1 gram of the substance in acetic acid was oxidised with an acetic acid solution of chromium trioxide, and the product poured into water. The resinous mass was dried and then sublimed, and the sublimate was proved to be anthraquinone by the method of mixed melting points.

The *diacetyl* derivative was prepared by heating 1 gram of the substance with 10 c.c. of acetic anhydride and four drops of pyridine under reflux for an hour. The product was poured into water and neutralised with sodium carbonate. The viscous mass solidified, and, after being fractionally crystallised from dilute alcohol, melted at 92° (Found: C=85·3; H=7·4. $C_{28}H_{24}O_2$ requires C=85·7; H=6·8 per cent.).

Dimethyl-9:10-*ditolyl*-9:10-*dihydroanthracene*.—This condensation was performed as in the preceding case, the catalyst being prepared from 1 gram of aluminium, 20 grams of mercuric chloride, and 15 c.c. of toluene. Chloroform (1 mol. for 2 mols. of toluene) was added through the condenser, and finally the reaction was completed at 70°. The oily product obtained after the decomposition of the mixture with ice, after being freed from chloroform and toluene, solidified when kept in a vacuum desiccator, and when crystallised from dilute acetic acid melted at 215° (Found: C=92·0; H=7·9. $C_{30}H_{28}$ requires C=92·7; H=7·3 per cent.).

Dimethyl-9:10-*diphenyl*-9:10-*dihydroanthracene*.—The catalyst, prepared from 8 c.c. of toluene, 0·5 gram of aluminium, and 10 grams of mercuric chloride, was treated with 4 c.c. of benzylidene chloride, the reaction being completed by heating at 60—70° for two hours. The oily product obtained after the usual treatment was dried and distilled under diminished pressure, when some oily matter passed over, and the residue solidified. This was extracted with hot alcohol, and, on concentration, a product was obtained which, after crystallisation from acetic acid, melted at 185° (Found: C=92·8; H=7·0. $C_{28}H_{24}$ requires C=93·3; H=6·7 per cent.).

9:9:10:10-*Tetraphenyl*-9:10-*dihydroanthracene*.—Eight c.c. of carbon tetrachloride were added to the catalyst, prepared from 20 c.c. of benzene, 1 gram of aluminium, and 20 grams of mercuric chloride, and the whole was kept at 50—60° for two hours, and then at 70° for an hour. After decomposing the product with ice and filtering, the dried residue was extracted with carbon disulphide, from which some of the tetraphenyl derivative was obtained. The filtrate separated into two layers, and the benzene layer, on evaporation, gave a further quantity of the substance, which, when crystallised from dilute acetone, melted at 159° (Found: C=94·0; H=6·8. $C_{38}H_{28}$ requires C=94·2; H=5·8 per cent.). The same compound was obtained by adding 5 c.c. of benzotrichloride, in the course of half an hour, to the catalyst, prepared from 15 c.c. of benzene, 1 gram of aluminium, and 20 grams of mercuric chloride. The product, isolated as above, melted at 159° (Found: C=94·02; H=5·1. Calc.: C=94·2; H=5·8 per cent.).

ω-*Nitrotriphenylmethane*.—Five c.c. of chloropicrin were used with 20 c.c. of benzene. The mixture was warmed first in a tepid-water bath and then for a few hours at 45°. The product was decomposed with ice, distilled in a current of steam, and the residue filtered, dried, and extracted with much boiling alcohol. This, on concentration, deposited ω-nitrotriphenylmethane, which, on recrystallisation from alcohol, melted and decomposed at 145° (Found: C=78·49; H=5·54; N=4·5. Calc.: C=78·8; H=5·1; N=4·8 per cent.).

In conclusion, I wish to express my best thanks to Sir P. C. Rây for the interest he has taken in the work, and to Mr. M. L. Dey for his criticisms and suggestions.

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CXLIV.—*The Freezing Point of Wet Benzene, and the Influence of Drying Agents.*

By Nevil Vincent Sidgwick.

During the purification of benzene by freezing for cryoscopic purposes, irregularities were observed in the freezing points of successive fractions, which were found to be due to traces of water absorbed from the air. This suggested the determination of the maximum depression of the freezing point of benzene by water. In a previous paper (T., 1915, **107**, 675), it was stated that this depression amounts to 0·042°, but later work has shown that the readiness with which benzene absorbs water from the air had been underestimated, and that the original benzene was not really dry. If proper precautions are taken to dry the benzene, its freezing point is lowered 0·100° by the addition of excess of water.*

This affords a convenient method for determining the efficiency of various drying agents. If the wet benzene is shaken with a solid dehydrating agent, which is insoluble in it, until a constant freezing point is obtained, the ratio of the depression observed in the presence of the drying agent to that produced by pure water is a measure of the lowering of the vapour pressure of the water by the latter, and hence of the efficiency of the drying agent. This efficiency must be the same (at temperatures near 5°) for a solution in any solvent in which the drying agent is insoluble.

Experimental.

Two samples of benzene, each about a litre, were used: one (*A*) was kindly given me by Dr. Hewitt and Mr. W. J. Jones; it was of English origin, and had been purified by them. The other (*B*) was Kahlbaum's purest. Neither gave more than the faintest trace of the indophenine reaction.

These were further purified separately by repeated freezing. In the later stages, irregularities of several hundredths of a degree were observed in the freezing points, which disappeared when the measurements were made in the presence of potassium carbonate.

When the freezing points appeared to be constant, the benzene

* After this work was finished, a paper appeared by Richards, Carver, and Schumb (*J. Amer. Chem. Soc.*, 1919, **41**, 2024), in which two experiments are described on the depression of the freezing point of pure benzene by water, giving the values 0·093° and 0·096°: mean 0·095°. This is in satisfactory agreement with the value 0·100° adopted in the present paper.

was still further purified by the method described by Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825) and by Richards and Barry (*ibid.*, 1915, **37**, 993). It was boiled for some hours with clean sodium (previously washed with the benzene) in a flask with a bent reflux condenser and drying tube. The condenser was then inclined downwards and connected to the side-tube of a carefully dried Beckmann apparatus. A steady stream of dried air was passed into the apparatus through the sheath of the stirrer, which was expanded into a bulb in the usual way, to prevent moist air from being drawn in when the stirrer was raised. It is essential that the access of moist air should be prevented; in one experiment the condenser tube was accidentally separated from the Beckmann apparatus for a minute, and this caused a drop in the freezing point of several thousandths of a degree. To the condenser tube between the water-jacket and the freezing-point apparatus, a rather narrow side-tube was sealed, so as to point downwards when the condenser was in position for distillation. The first runnings escaped through this tube, which was then closed by attaching a test-tube to it with an air-tight cork. The tube then filled up with liquid, and the rest of the distillate ran straight into the freezing-point apparatus.

Several readings of the freezing point having been taken, two or three drops of water were added, the tube was warmed with the hand and well stirred, and the freezing point again observed. This gave the difference between the freezing point of pure benzene and that of benzene saturated with water (the triple point, solid benzene–liquid benzene–water). Then about half a gram of dry, powdered potassium carbonate was added and thoroughly stirred, and the freezing point again taken. A smaller quantity of the salt was then added in the same way, and if this raised the freezing point, another small quantity was added; more than three additions were never required. This gives the temperature of the quadruple point, solid benzene–solid potassium carbonate–benzene solution–saturated aqueous solution of potassium carbonate. These operations were performed with successive frozen-out fractions of the purified benzene, and the results are given in the following table. The temperatures are referred to the arbitrary zero of the Beckmann thermometer, which remained constant during the experiments; each is the mean of several concordant readings, corrected for the temperature of the emergent stem. The fractions marked *A* are the English benzene, *B* the German; the index number following this shows the number of times it had been frozen out; thus, *A* 7 is the fraction obtained by freezing out the English benzene seven times.

Fraction.	I. Dried by sodium.	II. With water.	III. Wet, with potassium carbonate.	I.—II.	III.—II.
A 7	3·120°	3·021°	3·080°	0·099°	0·059°
A 7	3·121	3·021	3·081	0·100	0·060
A 8	—	3·023	3·083	—	0·060
A 9	3·119	3·021	—	0·098	—
B 6	3·115	3·015	3·075	0·100	0·060
B 7	—	3·020	3·081	—	0·061
B 8	3·121	3·022	—	0·099	—
B 8	—	3·022	3·081	—	0·061
			Means *A*....	0·099	0·060
			B....	0·100	0·061

The freezing point is thus lowered 0·100° by saturation with water. If the molecular weight of the dissolved water is 18, its solubility at 5·4° (assuming the cryoscopic constant 51°) must be 0·035 gram per 100 grams of benzene. Groschuff (*Zeitsch. Elektrochem.*, 1911, **17**, 348) found that 100 grams of benzene at 3° dissolve 0·030 gram of water, and at 23° 0·061, which would mean about 0·032 gram at 5·4°, agreeing with the observed depression for a molecular weight of 18. The value 0·24 gram in 100 grams at 22° given by Herz (*Ber.*, 1898, **31**, 267) is presumably erroneous.

On the addition of potassium carbonate, water is withdrawn from the benzene to form a saturated solution of the salt, the vapour pressure of which is lower than that of pure water; the concentration of the benzene solution diminishes and its freezing point rises by 0·061°, being 0·039° lower than that of pure benzene.

Other dehydrating agents were then examined in the same manner. Carefully dried and powdered specimens of sodium sulphate, copper sulphate, and calcium chloride were used, and also powdered sodium hydroxide and pure phosphoric oxide; this last blackens rapidly in impure benzene, but remains quite colourless in the pure liquid. All these compounds differ from potassium carbonate in forming hydrates with the water, and it is perhaps for this reason that some of them, especially copper sulphate, act more slowly, and must be stirred with the liquid for some time before their full effect appears. In these experiments, the benzene was not in each case distilled over sodium, but a mixture of the fractions *A* 9 and *B* 8, which had been so treated, was saturated with water, and after its freezing point had been measured it was dried with the salt, and the rise of freezing point so produced was observed.

Drying agent.	Elevation of freezing point.	Depression by water + agent.
None	—	0·100°
Sodium sulphate	0·024°	0·076
Potassium carbonate	0·061	0·039
Copper sulphate	0·089	0·011
Calcium chloride	0·091	0·009
Sodium hydroxide............	0·098	0·002
Phosphoric oxide	0·100	0·000

The removal of water by phosphoric oxide seems to be quite complete.

The middle column in the above table gives a measure of the relative efficiency of the drying agents examined. If water in benzene solution is unimolecular, its concentration in the solution is proportional to the pressure of its vapour, and hence the depression given in the last column is directly proportional to the vapour pressure of the system, drying agent–lowest hydrate (or saturated solution in the case of potassium carbonate)–vapour.

The last column in the following table gives the values of the tension of aqueous vapour calculated on this hypothesis. The preceding column gives the actual freezing points, based on the revised value given by Richards, Carver, and Schumb (see footnote on p. 1340) for pure benzene.

System.	Freezing point.	Tension of aqueous vapour in mm.
Benzene, pure	5·493°	—
,, saturated with water ...	5·393	6·73
,, wet + sodium sulphate...	5·420	5·11
,, ,, + potassium carbonate	5·454	2·62
,, ,, + copper sulphate ...	5·482	0·74
,, ,, + calcium chloride ...	5·484	0·61
,, ,, + sodium hydroxide	5·491	0·13
,, ,, + phosphoric oxide .	5·493	0·00

The relative efficiency of these substances is, of course, the same for drying solutions in any other solvents in which they do not dissolve.

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OXFORD.
[*Received, August 13th*, 1920.]

CXLV.—*Studies in the Acenaphthene Series. Part I. The Conversion of* o-*Nitroamines into* iso*Oxadiazole Oxides.*

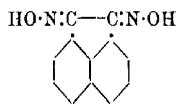
By Frederick Maurice Rowe and John Stanley Herbert Davies.

In four previous communications (T., 1912, **101**, 2452; 1913, **103**, 897, 2023; 1917, **111**, 612), one of us has shown that many *o*-nitroamines in the benzene and naphthalene series are converted into furoxans (furazan oxides or *iso*oxadiazole oxides) when oxidised in alkaline solution with sodium hypochlorite. In order further to test the generality of this reaction, we have now carried out similar experiments in the acenaphthene series. Sachs and Mosebach (*Ber.*, 1911, **44**, 2852) have shown that whilst the direct nitration of acenaphthene yields a dinitro-derivative which contains the nitro-groups in the 3:4- or peri-position, the reduction of 3-nitroacenaphthene, followed by acetylation, nitration, and hydrolysis of the resulting nitroacetylaminoacenaphthene, gives rise to 2-nitro-3-aminoacenaphthene. The latter compound, which contains the nitro- and amino-groups in the ortho-position with respect to one another, has now been submitted to the hypochlorite oxidation. It is interesting to note that, although the yield of the oxidation product was low, the methylene groups of the acenaphthene ring remained unaffected, and *acenaphthene*-2:3-iso*oxadiazole oxide* was obtained. The corresponding compounds in the benzene and naphthalene series possess a characteristic almond odour, and are readily volatile with steam, but this compound is odourless and non-volatile. It is reduced by hydroxylamine to *acenaphthene*-2:3-*quinonedioxime*, which may be converted into *acenaphthene*-2:3-iso*oxadiazole* in the usual manner, although the yield is not good.

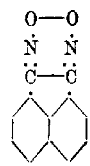
An attempt to reduce 2-nitro-3-acetylaminoacenaphthene to the corresponding nitroso-compound in a similar manner to that used by one of us for the preparation of *o*-nitrosoacetanilide (*loc. cit.*), in order to prepare acenaphthene-2:3-*iso*oxadiazole from it by the alkaline hypochlorite oxidation, proved unsuccessful.

o-Quinonedioximes are readily converted into *iso*oxadiazole oxides by oxidation in alkaline solution with sodium hypochlorite, and consequently it was to be expected that the oxidation of acenaphthene-7:8-quinonedioxime in this manner would yield an *iso*oxadiazole oxide derivative of acenaphthene of a different type

from that already described. This, in fact, proved to be the case, and *acenaphthene*-7:8-iso*oxadiazole oxide* was obtained. On the other hand, acenaphthene-7:8-quinonedioxime resisted all attempts to convert it into acenaphthene-7:8-*iso*oxadiazole by the removal of water. It remained unaffected by prolonged boiling with aqueous sodium hydroxide, and when heated with aqueous sodium hydroxide in a sealed tube, decomposition occurred, with the formation of acenaphthenequinone and ammonia, whilst no better result was obtained by heating with water in a sealed tube. Moreover, treatment of the diacetyl derivative of acenaphthene-7:8-quinonedioxime with sodium hydroxide merely resulted in hydrolysis, with no dehydration. This failure to dehydrate acenaphthene-7:8-quinonedioxime suggests that this compound most probably has the structure of a β(anti)-dioxime (I). The failure of this compound



(I.)



(II.)

to give a nickel salt when treated with ammoniacal nickel solutions, as described by Atack (T., 1913, **103**, 1317) in an investigation of the three stereoisomeric benzildioximes, further supports this view.

The preparation of acenaphthene-7:8-*iso*oxadiazole oxide was of interest in view of the fact that Francesconi and Pirazzoli (*Gazzetta*, 1903, **33**, i, 36) prepared a compound by boiling acenaphthene-7:8-quinonedioxime with amyl nitrite, to which the peroxide formula (II) was provisionally assigned. This compound is described as forming reddish-brown crystals, decomposing at 90° and melting at 140°. It is soluble in organic solvents, with decomposition, forming a black substance which does not melt at 260°. We therefore prepared a quantity of this compound in order to determine whether it was identical or not with acenaphthene-7:8-*iso*oxadiazole oxide. After repeated crystallisation, it was obtained finally in small, brown needles, decomposing at 190° and melting at 206·5°, and, when pure, it was not decomposed by organic solvents. This substance possesses quite different properties from those of acenaphthene-7 : 8-*iso*oxadiazole oxide; for example, the former dissolves in cold aqueous sodium hydroxide with a pale yellow colour, whilst the latter is quite insoluble in alkali hydroxides, and, moreover, is readily reduced to acenaphthene-7:8-quinonedioxime by hydroxylamine. It is evident that the two

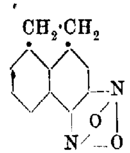
compounds are not identical, and Francesconi and Pirazzoli's compound was not examined more closely, but, in view of its properties, it seemed doubtful whether it possesses the peroxide formula assigned to it by these authors.

When the present investigation was commenced, the literature contained no reference to nitro-derivatives of acenaphthenequinone, and it was decided to fill in this blank. After the necessary experiments had been carried out, however, these compounds were described by Mayer and Kauffmann (*Ber.*, 1920, **53**, [*B*], 296).

The product of mononitration is 3-nitroacenaphthenequinone melting at 218° (M. and K. give 199°), which forms a monophenylhydrazone melting at 234—235° (M. and K. give 186°), and the product of dinitration is 3:4-dinitroacenaphthenequinone melting and decomposing above 300°, which forms a *monophenylhydrazone* darkening at 260° and melting at 287°.

In conclusion, it appeared of interest to ascertain whether the nitro-derivatives of acenaphthenequinone could be prepared by the oxidation of the nitro-derivatives of acenaphthene, as the preparation of a substituted acenaphthenequinone by the oxidation of the corresponding derivative of acenaphthene has been effected only in one instance, namely, by Graebe (*Annalen*, 1903, **327**, 77), who found that 5-bromoacenaphthene was oxidised either to bromoacenaphthenequinone or bromonaphthalic acid, according to the conditions used. Experiments were made with 3-nitroacenaphthene, using a series of oxidising agents under a variety of conditions, but it was found that this compound either remained unaffected or was oxidised to 4-nitronaphthalene-1:8-dicarboxylic acid melting, as anhydride, at 229—230° (Graebe gives 220°), and in no case could we isolate any 3-nitroacenaphthenequinone.

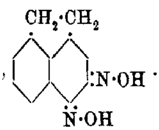
EXPERIMENTAL.

Acenaphthene-2:3-iso*oxadiazole Oxide*, 

The 2-nitro-3-aminoacenaphthene required was obtained by Sachs and Mosebach's method (*loc. cit.*). Acenaphthene (m. p. 96°) was nitrated in glacial acetic acid suspension, and the product extracted with light petroleum (b. p. 90°), in which any dinitro-derivative formed simultaneously is insoluble. The yield of 3-nitroacenaphthene, yellow needles, melting at 101—102°, was 89 per cent. (S. and M. give 84 per cent.). The reduction of the

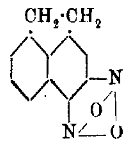
nitro-compound is best effected in aqueous-alcoholic solution with sodium hyposulphite. The yield of 3-aminoacenaphthene, almost colourless, silky needles melting at 104—105°, was 71 per cent. (S. and M. give about 77 per cent. of an almost pure product). The monoacetyl derivative is best prepared with acetyl chloride. After repeated crystallisation from methyl alcohol, 3-acetylamino-acenaphthene, glistening needles melting at 238°, was obtained in a yield of 92 per cent. The melting point of this compound is greatly affected by traces of impurities; thus Quincke (*Ber.*, 1885, **21**, 1457) gives 176°, Graebe (*Annalen*, 1903, **327**, 77) gives 186°, and Sachs and Mosebach (*loc. cit.*) give 192°. A number of nitrations were carried out, but the yield was always low, owing to oxidation; 2-nitro-3-acetylaminoacenaphthene, golden-yellow needles melting at 255°, was obtained in a yield of 35 per cent. (S. and M. give 253°; yield, about 54 per cent.). When hydrolysed with alcoholic hydrochloric acid, 2-nitro-3-aminoacenaphthene, blunt, red prisms with a green lustre, melting at 222°, was obtained in an almost theoretical yield (S. and M. give 85 per cent.).

The oxidation of 2-nitro-3-aminoacenaphthene was best effected by the addition of an excess of alkaline sodium hypochlorite to a hot alcoholic solution of the nitroamine. The mixture was boiled for a short time, cooled, diluted with water, and the precipitate collected. When crystallised from alcohol or acetic acid, *acenaphthene-2:3-isooxadiazole oxide* forms pale brown needles melting at 177—178°. A yield of 50 per cent. was obtained. The compound is odourless, non-volatile with steam, and, when heated with zinc dust, ammonia is evolved and naphthalene formed (Found: N = 13·32. $C_{12}H_8O_2N_2$ requires N = 13·2 per cent.).

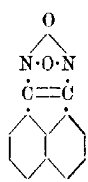
Acenaphthene-2:3-quinonedioxime, 

This compound was formed by the reduction of acenaphthene-2:3-*iso*oxadiazole oxide with an excess of hydroxylamine (at least four molecular proportions). It was difficult to isolate, owing to the ease with which it was converted into acenaphthene-2:3-*iso*-oxadiazole. The best results were obtained by dissolving the *iso*oxadiazole oxide in alcohol and adding an aqueous solution of hydroxylamine hydrochloride, after which the mixture was rendered alkaline with sodium hydroxide at 50° and heated for twenty minutes on the water-bath at 60°. The brown solution was cooled, acidified with acetic acid, and diluted with water. The

precipitate was extracted with dilute sodium hydroxide, filtered, and the filtrate precipitated with acetic acid. The quinonedioxime separates as a colloidal precipitate, which it was not found possible to crystallise. When dry, it forms a brown, amorphous powder, which decomposes when heated and does not melt below 280°, sparingly soluble in organic solvents, but dissolving readily in alkali hydroxides with a brown colour. On oxidation with sodium hypochlorite, it is reconverted into acenaphthene-2:3-*iso*oxadiazole oxide, and, on heating with sodium hydroxide, it is converted into acenaphthene-2:3-*iso*oxadiazole (Found: N = 13·34. $C_{12}H_{10}O_2N_2$ requires N = 13·08 per cent.).

Acenaphthene-2:3-iso*oxadiazole*,  .

Acenaphthene-2:3-quinonedioxime was dissolved in dilute sodium hydroxide and distilled in a current of steam. The product, after recrystallisation from acetic acid, forms yellow needles melting at 143—144°. It is only slightly volatile with steam, and the yield is low, owing to the formation of a large proportion of a black, non-volatile decomposition product (Found: N = 14·45. $C_{12}H_8ON_2$ requires N = 14·28 per cent.).

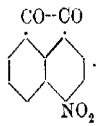
Acenaphthene-7:8-iso*oxadiazole Oxide*,  .

The acenaphthene-7:8-quinonedioxime required was obtained by Francesconi and Pirazzoli's method (*loc. cit.*). Five grams of powdered acenaphthenequinone (m. p. 259°) were suspended in 450 c.c. of boiling alcohol, and 3·8 grams of hydroxylamine hydrochloride dissolved in the minimum quantity of water added. The mixture was boiled for one hour under reflux, and the major portion of the alcohol removed by distillation. The product, colourless needles, melting and decomposing at 220°, was obtained in almost theoretical yield.

An excess of alkaline sodium hypochlorite was added to a solution of acenaphthene-7:8-quinonedioxime in dilute sodium hydr-

oxide, and the mixture boiled. A yellow precipitate separated, which changed in colour through red to pale pink, and boiling was continued until no further colour change occurred. After crystallising twice from alcohol, the compound forms pale pink needles melting at 199°.

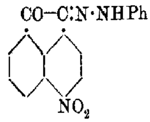
Acenaphthene-7 : 8-iso*oxadiazole oxide* is reduced by hydroxylamine to acenaphthene-1 : 2-quinonedioxime (Found: N = 12·96. $C_{12}H_6O_2N_2$ requires N = 13·30 per cent.).

3-*Nitroacenaphthenequinone*,  .

Ten grams of acenaphthenequinone, dissolved in 50 c.c. of concentrated sulphuric acid, were nitrated in the cold with one molecular proportion of nitric acid (D 1·51) mixed with twice its volume of concentrated sulphuric acid. At the end of the addition, the mixture was warmed for one hour at 30° and poured on ice. The yield was 92 per cent. Purification by immediate crystallisation proved unsatisfactory, and the best results were obtained by a mild oxidation, which removed the impurities without affecting the nitroquinone. The product (11·5 grams) was dissolved in glacial acetic acid, the solution filtered, and 5 grams of powdered sodium dichromate were slowly added to the filtrate. The mixture was heated on a boiling-water bath for a quarter of an hour and poured into water. After repeated crystallisation from acetic acid, 3-nitroacenaphthenequinone forms yellow needles melting at 218°. It dissolves in sodium hydrogen sulphite with a red colour, and dissolves in dilute alkali hydroxides with a brown colour, whilst it is converted by hot concentrated aqueous sodium hydroxide into 2(or 3)-nitronaphthaldehydic acid, as described by Mayer and Kauffmann (*loc. cit.*).

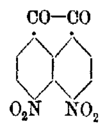
3-Nitroacenaphthenequinone is oxidised by sodium dichromate and acetic acid to 4-nitronaphthalene-1 : 8-dicarboxylic anhydride, almost colourless needles, melting at 229—230°, identical with the product obtained by a similar oxidation of 3-nitroacenaphthene. When distilled with lime, α-nitronaphthalene is obtained (Found: N = 5·93. Calc.: N = 6·17 per cent.).

3-*Nitroacenaphthenequinone*-7(or 8)-*monophenylhydrazone*,



A cold glacial acetic acid solution of 5 grams of 3-nitroacenaphthenequinone was mixed with a cold glacial acid solution of 2·4 grams of phenylhydrazine, and the dark red mixture was left at the ordinary temperature for half an hour, with frequent shaking. The monophenylhydrazone separates as a maroon-coloured precipitate. After several crystallisations from pyridine, the product forms reddish-brown needles melting at 234—235° (Found: N = 13·22. Calc.: N = 13·25 per cent.).

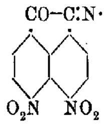
3 : 4-*Dinitroacenaphthenequinone*,



Ten grams of acenaphthenequinone, dissolved in 150—200 c.c. of concentrated sulphuric acid, were nitrated by the addition of a mixture of 7 c.c. of nitric acid (D 1·51) and 20 c.c. of concentrated sulphuric acid. The mixture was cooled at first, then warmed to 80°, and poured on ice. The product, after extraction with very dilute sodium carbonate, crystallised from nitric acid in orange-yellow needles melting and decomposing above 300°. It dissolves with a red colour, and is soluble in alkali hydroxides with a reddish-brown colour.

3 : 4-Dinitroacenaphthenequinone is oxidised by sodium dichromate and acetic acid to 4 : 5-dinitronaphthalene-1 : 8-dicarboxylic anhydride, almost colourless needles, melting and decomposing above 310°, identical with the product obtained by the oxidation of 3 : 4-dinitroacenaphthene. No dinitronaphthalene is obtained when distilled with lime, as 1 : 8-dinitronaphthalene decomposes below its boiling point (Found: N = 10·17. Calc.: N = 10·29 per cent.).

3 : 4-*Dinitroacenaphthenequinone-7-monophenylhydrazone*,



An acetic acid solution of 2 grams of phenylhydrazine was added to an acetic acid solution of 5 grams of 3 : 4-dinitroacenaphthenequinone at 50°, and the mixture allowed to remain for one hour at the ordinary temperature. On dilution with water, the product separated as a reddish-yellow precipitate. It crystallises from acetic acid in brown, glistening plates, darkening above 260° and melting at 287° (Found: N = 15·57. $C_{18}H_{10}O_5N_4$ requires N = 15·47 per cent.).

In conclusion, we desire to express our thanks to Messrs. Hardman and Holden, Ltd., who have kindly supplied us with the acenaphthene required in this investigation.

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MANCHESTER. [*Received, October 8th*, 1920.]

CXLVI.—*Diethylenetriamine and Triethylenetetramine*.

By ROBERT GEORGE FARGHER.

THE interaction of ethylene dichloride and a large excess of ammonia has been investigated by Kraut (*Annalen*, 1882, **212**, 253), who considered that it led almost entirely to ethylenediamine, although the reaction of the alcohol-soluble portion of the mixed hydrochlorides with potassium bismuth iodide indicated that a small proportion of piperazine was formed.

The author had occasion to prepare several kilograms of ethylenediamine, essentially by Kraut's method, and it was thought to be of interest to investigate in more detail the other products of the reaction. The hydrochlorides obtained by evaporation of the product were converted into the corresponding bases and fractionally distilled. The portion of higher boiling point consisted mainly of diethylenetriamine, whilst there was also produced, although in much smaller quantity, triethylenetetramine. The intermediate

cyclic bases, piperazine and triethylenetriamine, appeared to be absent. Of the two bases isolated, the former was first obtained by Hofmann (*Proc. Roy. Soc.*, 1860, **10**, 619), admixed with triethylenetriamine, by the action of ammonia on ethylene dibromide, and was separated by the more sparing solubility of its platinichloride; the second base he obtained by the interaction of ethylenediamine and ethylene dibromide (*loc. cit.*), ethylene dibromide and alcoholic ammonia (*loc. cit.*), and ethylenediamine and ethylene dichloride (*Ber.*, 1890, **23**, 3712). For purposes of identification and characterisation, a number of derivatives of both have been prepared.

It is of interest to record that the direct union of ethylene with chlorine, utilised in the preparation of the ethylene dichloride required in the present experiments, shows that electrolytic chlorine from a freshly charged cylinder is considerably more active, under identical conditions, than that prepared from bleaching powder. This is in accordance with the view that chlorine is activated by exposure to an electric discharge (compare Kellner, *Zeitsch. Elektrochem.*, 1902, **8**, 500; Russ, *Monatsh.*, 1905, **26**, 627; Briner and Durand, *Zeitsch. Elektrochem.*, 1908, **14**, 706), and that chlorine prepared by electrolysis is more active towards hydrogen (Chapman and MacMahon, T., 1909, **95**, 135).

Contrary to the experience of Russ (*Chem. Ind.*, 1908, **31**, 131), the increased activity is not lost by heating or by contact with water or solutions of such salts as calcium chloride or potassium chlorate. As an example, the fractionation of the products of two experiments may be cited, the results being representative of many others. In the first, using chlorine from bleaching powder, 92 per cent. of the product distilled between 84° and 88°, only 4 per cent. passing over at a higher temperature. In the second, using chlorine from a freshly charged cylinder, only 7 per cent. distilled between 80° and 90°, 25 per cent. passing over between 90° and 100°, 50 per cent. between 100° and 120°, and 14 per cent. above that temperature.

As an alternative to the Kraut process, the reduction of aminoacetonitrile was investigated. The catalytic reduction with hydrogen under pressure in the presence of nickel suboxide had already been claimed to yield ethylenediamine (Brit. Pat. 21883 of 1914). Reduction with sodium and alcohol, zinc and hydrochloric acid, and iron and hydrochloric acid also yielded ethylenediamine, although, as hydrolysis of the nitrile proceeded simultaneously, the yield never exceeded 33 per cent. of the theoretical.

EXPERIMENTAL.

Separation of the Bases.

The bases obtained by distilling the mixed hydrochlorides with solid sodium hydroxide, preferably under somewhat diminished pressure, were freed from water by means of solid sodium hydroxide* and then distilled, first under the ordinary pressure to remove most of the ethylenediamine hydrate, and then under 20 mm. There was first obtained a small fraction boiling below 100° which consisted almost entirely of ethylenediamine, and after this most of the remaining oil passed over between 100° and 120°. The temperature then rose to 155° without remaining constant at any intermediate point, and a fraction was collected boiling between 155° and 165°/20 mm. The first fraction proved to consist almost entirely of diethylenetriamine, which distilled at 109°/20 mm. The second fraction on redistillation boiled at 157°/20 mm., and proved to be triethylenetetramine.

Diethylenetriamine and its Derivatives.

Diethylenetriamine dissolves in water with the evolution of heat and apparent formation of a hydrate. The aqueous solution of the base gives copious, white precipitates with potassium mercuri-iodide, mercuric chloride, or phosphotungstic acid, soluble in excess of the base, but no precipitate with tannic acid. It reduces silver nitrate on warming. The alcoholic solution yields an insoluble carbonate when treated with carbon dioxide. Attempts to titrate the base with standard acid, using methyl-orange, Congo-red, litmus, or cochineal as indicator, proved unsuccessful, as no definite end-point could be obtained. For analysis, it was finally distilled over a little solid sodium hydroxide, and was afterwards kept out of contact with moisture or carbon dioxide (Found: C=46·3; H=13·1; N=40·3. Calc.: C=46·6; H=12·7; N=40·75 per cent.).

The trihydrochloride (Hofmann, *Proc. Roy. Soc.*, 1862, **11**, 420) separates from aqueous alcohol containing excess of hydrogen chloride in bunches of feathery needles which melt at 233° (corr.), sintering from 225° (Found: Cl=50·1, 50·2; N=19·6. Calc.: Cl=50·1; N=19·8 per cent.).

The *tripicrate* is sparingly soluble, even in boiling water, and crystallises in glistening, flattened prisms which melt and decom-

* It is not sufficient simply to distil over sodium hydroxide.

pose at 212° (corr.) (Found: N = 21·5. $C_4H_{13}N_3,3C_6H_3O_7N_3$ requires N = 21·3 per cent.).

The *oxalate* crystallises from water, in which it is readily soluble, in flattened prisms containing $4H_2O$. After drying at 110°, it melts and effervesces at 183° (corr.) (Found: loss at 110° = 13·0. $2C_4H_{13}N_3,3C_2H_2O_4,4H_2O$ requires H_2O = 13·1 per cent. In dried substance, N = 17·5. $2C_4H_{13}N_3,3C_2H_2O_4$ requires N = 17·6 per cent.).

The *citrate* is practically insoluble in alcohol, ether, or chloroform, but readily so in water, from which it separates in well-defined, rhombic prisms containing $1H_2O$. After drying at 110°, it melts and effervesces at 206°, sintering from 200° (Found: loss at 110° = 6·3. $C_4H_{13}N_3,C_6H_8O_7,H_2O$ requires H_2O = 5·8 per cent.). In dried substance, N = 14·4. $C_4H_{13}N_3,C_6H_8O_7$ requires N = 14·2 per cent.).

The *triacetyl* derivative is practically insoluble in alcohol or light petroleum, but very readily soluble in water. It separates from 70 per cent. alcohol as a felted mass of needles, which, in contact with the solvent, change to well-defined prisms melting at 220° (corr.) (Found: N = 18·0. $C_{10}H_{19}O_3N_3$ requires N = 18·3 per cent.).

The *tribenzoyl* derivative is very sparingly soluble in ether, or light petroleum, but readily so in water or alcohol. From chloroform it separates in small, flattened prisms containing one molecule of the solvent, which is gradually lost on exposure to the air, but regained on keeping over chloroform in a desiccator. After removal of the solvent of crystallisation, it melts at 166° (corr.) (Found: $CHCl_3$ = 21·9. After forty-eight hours, this had diminished to 16·1 per cent. In dried substance, C = 71·9; H = 6·1; N = 10·1. $C_{25}H_{25}O_3N_3$ requires C = 72·2; H = 6·1; N = 10·1 per cent.).

Triethylenetetramine and its Derivatives.

Triethylenetetramine behaves very similarly to diethylenetriamine in its reactions, dissolving in water with evolution of heat, forming an insoluble carbonate when carbon dioxide is passed through its alcoholic solution, and giving precipitates with potassium mercuri-iodide, mercuric chloride, and phosphotungstic acid. It reduces silver nitrate on warming. For analysis, it was finally distilled over solid sodium hydroxide (Found: C = 48·8; H = 12·7; N = 38·0. Calc.: C = 49·3; H = 12·4; N = 38·3 per cent.).

The tetrahydrochloride separates from 70 per cent. alcohol containing excess of hydrogen chloride in minute needles (Found: Cl = 48·0. Calc.: Cl = 48·5 per cent.)

The *tetrapicrate* is very sparingly soluble, even in boiling water, from which it separates in fern-like clusters of minute, rhombic prisms melting and decomposing at 240° (corr.) (Found: N = 20·7. $C_6H_{18}N_4,4C_6H_3O_7N_3$ requires N = 21·1 per cent.).

The *hydrogen oxalate* is sparingly soluble in water, and separates in glistening needles, which effervesce at 243° (corr.) and contain $1H_2O$ (Found: loss at 110° = 3·0. $1H_2O$ requires 3·2 per cent. In dried material, C = 33·3; H = 5·5; N = 10·9. $C_6H_{18}N_4,4C_2H_2O_4$ requires C = 33·2; H = 5·2; N = 11·1 per cent.).

The tetrabenzoyl derivative dissolves sparingly in water or alcohol, but readily in chloroform. It separates from a mixture of chloroform and alcohol in fine, powdery crystals melting at 238° (corr.) (Hofmann, *Ber.*, 1890, **23**, 3717, gives 228—229°) (Found: C = 72·8; H = 6·5; N = 9·9. Calc.: C = 72·55; H = 6·1; N = 10·0 per cent.).

Methyleneaminoacetonitrile and Aminoacetonitrile.

Methyleneaminoacetonitrile was prepared substantially by the process described by Klages (*Ber.*, 1903, **36**, 1511). It was found, however, that the time of addition of the cyanide could be materially decreased without detriment to the yield so long as the temperature was maintained below 10° during the first half of the addition, and below 15° during the second. It was readily converted into aminoacetonitrile hydrochloride by shaking with the calculated quantity of *N*-alcoholic hydrogen chloride, the yield amounting to 90 per cent. of the theoretical.

Reduction of Aminoacetonitrile Hydrochloride.

With Sodium and Alcohol.—Twenty grams of the hydrochloride were added to 60 c.c. of alcohol in which 5 grams of sodium had previously been dissolved, 80 grams of sodium were added, and, after the first violent reaction had ceased, the mixture was heated on the water-bath, 250 c.c. of alcohol being gradually added. After about an hour, most of the alcohol was removed by distillation, a little 90 per cent. alcohol added to ensure that the sodium was all used, water added, and the mixture transferred to a copper flask and distilled to dryness under somewhat diminished pressure. The distillate was boiled to remove ammonia, neutralised with hydrochloric acid, and concentrated to crystallisation. The yield of ethylenediamine dihydrochloride varied from 25 to 33 per cent. of the theoretical.

With Iron and Hydrochloric Acid.—Five grams of aminoaceto-

nitrile hydrochloride were dissolved in 100 c.c. of water, 16 grams of iron filings added, and 50 c.c. of hydrochloric acid added slowly during an hour, with shaking. At the end of the reaction, the product was evaporated to dryness, distilled from a copper flask with sodium hydroxide, and the base in the distillate isolated as hydrochloride. The yield amounted to 10 per cent. of the theoretical.

With Zinc and Hydrochloric Acid.—To a solution of 6·8 grams of the hydrochloride in 100 c.c. of water, 30 grams of zinc were added, and 70 c.c. of concentrated hydrochloric acid added, as above, the product being then treated as in the previous reduction. The yield of ethylenediamine dihydrochloride amounted to 25 per cent. of the theoretical.

In conclusion, the author would thank Messrs. R. R. Baxter and J. A. Goodson for assistance in the preparation of the ethylene dichloride and ethylenediamine which formed the basis of the investigation.

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CXLVII.—*The Constitution of Carbamides. Part XIII. The Constitution of Cyanic Acid, and the Formation of Urea from the Interaction of Ammonia and Cyanic Acid at Low Temperatures.*

By EMIL ALPHONSE WERNER and WILLIAM ROBERT FEARON.

THE theory which has been put forward by one of us to explain the constitution of urea, and the mechanism of its formation from ammonium cyanate* (T., 1913, **103**, 1013, 2276; 1918, **113**, 84), is based, primarily, on the conception that cyanic acid, whether in the static condition or in solution, is an equilibrium mixture, represented thus:

$$\underset{\text{Stable only at low temperature.}}{\text{(enol-form) HO·CN}} \;\underset{\text{Promoted by fall of t°.}}{\overset{\text{Promoted by rise of t°.}}{\rightleftarrows}}\; \underset{\text{Stable at high temperature.}}{\text{HN:CO (keto-form).}}$$

Since cyanic acid is at all times very unstable, the stability referred to above is only relative. Permanent stability is only

attained by polymerisation, with the production of cyanuric acid from the keto-form and of cyamelide from the enol-form of the acid (*loc. cit.*).

Now, the ease with which ammonium cyanate is changed to urea is indicative of a close similarity in structure, and hence the constitution of cyanic acid is a question of paramount importance in solving the problem of the relation which exists between the two isomerides.

There are two reasons why previous investigators have given either little or no consideration to this important question, namely, the apparent uncertainty which has been assumed to exist as regards the nature of cyanic acid, and the general acceptance of the "carbamide" formula, which has all along masked the true relationship between urea and ammonium cyanate.

As a matter of fact, the constitution of cyanic acid is clearly indicated by (*a*) its polymerisation, and (*b*) its hydrolysis and behaviour towards ammonia at low temperatures.

(a) *Polymerisation of Cyanic Acid.*

Senier and Walsh (T., 1902, **81**, 290) showed that the spontaneous polymerisation of cyanic acid yielded a product which contained, in round numbers, 70 per cent. of cyanuric acid and 30 per cent. of cyamelide. This was the result of a single experiment, in which no particular effort was made to control the temperature at which polymerisation took effect.

If the theory of the polymerisation of cyanic acid which was propounded by one of us is sound (T., 1913, **103**, 1016),* and if cyanic acid is an equilibrium mixture, as indicated above, it follows that its composition at any particular temperature will be revealed by the relative proportions of the two polymerides formed. This inference, which was predicted when the theory was put forward, has now been verified by analyses of the products formed when liquid cyanic acid polymerised at different temperatures.

At zero the acid was stable for about four hours, provided it was not agitated, and it polymerised slowly. In order to obtain a reasonable control of the temperature at which polymerisation took place, only very small quantities of the acid were dealt with in each experiment (see experimental part).

The results were as follows:

* For the sake of brevity, the theory is not reproduced here; in order to appreciate the significance of the results obtained it is necessary to consult the paper on the mechanism of the polymerisation of cyanic acid to which reference is made.

TABLE I.

Temperature of polymerisation (approximate).	Weight of polymeride.	Cyanuric acid found.	Percentage composition of polymeride.	
			Cyamelide.	Cyanuric acid.
0°	0·53 gram.	0·216 gram	59·25	40·75
5	0·42 ,,	0·174 ,,	58·58	41·42
10	0·105 ,,	0·045 ,,	57·27	42·73
20	0·24 ,,	0·136 ,,	42·92	57·08

In several experiments, where the acid polymerised when the containing vessel was plunged into water at 20°, the temperature rose suddenly to about 70°, and the proportions of cyanuric acid formed were from 70 to 80 per cent. Since the latter acid is almost the sole product found when polymerisation takes place at high temperatures, as, for example, when urea is heated above its melting point (132°) (T., 1913, **103**, 2276), it follows that, under such conditions, cyanic acid is liberated in the keto-form. Liquid cyanic acid, on the other hand, must be an equilibrium mixture, the composition of which is a function of the temperature; thus, at 0°, it may be represented as approximately

$$\underset{\text{60 per cent.}}{\mathrm{HO{\cdot}CN}} \rightleftarrows \underset{\text{40 per cent.}}{\mathrm{HN{:}CO}}$$

(b) *Hydrolysis of Cyanic Acid, and its Reaction with Ammonia at Low Temperatures.*

Whenever urea is formed in a reaction where cyanic acid and ammonia are concerned, it has always been assumed that it must originate from the transformation of ammonium cyanate produced in the first instance. Since the difference between the two isomerides is nothing more than that of the products of the union of ammonia with the enol- and keto-forms, respectively, of cyanic acid, it is obvious that the above assumption is superfluous.

A quantitative study of the hydrolysis of cyanic acid has supplied convincing evidence that both isomerides are simultaneously formed when ammonia reacts with the acid at low temperatures. Not less than six consecutive changes are involved during the progress of this reaction, and these are conveniently divided into two groups, as follows:

Primary changes:

(1) $(\mathrm{HOCN} \rightleftarrows \mathrm{HNCO}) + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{NH_3}$.

(2) $\mathrm{HOCN} + \mathrm{NH_3} = \mathrm{NH_4{\cdot}OCN}$.

(3) $\mathrm{HN{:}CO} + \mathrm{NH_3} = \mathrm{HN{:}C}{<}^{\mathrm{NH_3}}_{\mathrm{O}}$.

Secondary changes:

(4) $NH_3 + CO_2 + H_2O = NH_4HCO_3$.
(5) Formation of biuret from interaction of urea and HNCO.
(6) Production of cyamelide.

The main question was to prove the validity of reaction (3). This was successfully accomplished when an approximately $N/4$-solution of cyanic acid was allowed to hydrolyse at 0°. Under such conditions, the secondary changes were almost completely suppressed up to the point at which the primary changes were completed. A solution of cyanic acid was prepared by the addition of the theoretical amount (62·5 c.c.) of N-nitric acid to 5·05 grams of pure potassium cyanate dissolved in 187·5 c.c. of water. The solution (250 c.c.) was prepared at 0°, and maintained at this point during all the analyses.

The following results were obtained with 25 c.c., taken at intervals of fifteen minutes (Expt. II).

TABLE II.

Time in minutes.	Cyanic acid present (free, and as NH_4OCN). Gram.	Urea formed (theoretical). Gram.		Urea found. Gram.
—	0·230*	—		—
15	0·195	0·024	Total urea at this stage =0·313.	0·018
30	0·165	0·045		0·038
45	0·129	0·070		0·063
60	0·109	0·084		0·081
75	0·101	0·090		0·087
90	0·094	0·094		0·089
1230	0·061	0·118		not estimated.

* 0·267 Gram is the theoretical amount, from the weight of potassium cyanate taken. The deficiency found at the outset was due to: (a) loss by volatilisation—the solution had a very pungent odour; (b) time elapsed during addition of nitric acid, and impossibility of avoiding to a small extent the change $HOCN + H_2O + HNO_3 = NH_4NO_3 + CO_2$.

The theoretical values for urea formed were calculated from the amounts of cyanic acid which had disappeared after each interval on the basis $2HNCO \longrightarrow CON_2H_4$.

It will be seen that, under the conditions stated, the hydrolysis of cyanic acid was comparatively slow; thus, about ninety minutes were required before all free acid had disappeared. At this stage the three primary reactions had been completed, hence there was no object in estimating urea formed beyond this point, since it could only then arise from the slow transformation of ammonium cyanate, as a result of its hydrolytic dissociation, thus:

$$NH_4OCN = NH_3 + HOCN \rightleftharpoons HNCO.$$

This is strikingly shown by the last result, where, in the interval between 90 and 1230 minutes, only 0·033 gram of cyanic acid (as ammonium cyanate) had been removed, and when this is considered in connexion with the fact that in 75 minutes from the commencement of the change 0·313 gram of urea was formed, there can be no doubt that the latter can only have been produced as the direct result of reaction (3). Now, after 75 minutes, when the disturbing effects of reaction (4) were just noticeable,* half of the solution (125 c.c.) had been used, that is, 1·15 grams of cyanic acid, capable of yielding 0·8 gram of either urea or ammonium cyanate, had taken part in the completion of reactions (1), (2), and (3). Hence (0·8—0·313) 0·487 gram of ammonium cyanate was formed, which shows that cyanic acid, in aqueous solution at 0°, had reacted with ammonia as a mixture of HOCN = 60·9 per cent. and of HNCO = 39·1 per cent., a result almost identical with that arrived at from the study of the polymerisation of the anhydrous acid at the same temperature.

As regards the secondary changes, the production of biuret confirms reaction (3), since it must be a sequence of it (compare Werner, T., *loc. cit.*; P., 1914, **30**, 262), and whilst its formation does not affect the above result as regards the proportion of cyanic acid which reacted as HN:CO, its presence was mainly responsible for the low values found for urea formed in the early stages of the reaction. In agreement with theory, the formation of biuret was largely confined to this period.

The production of a trace of cyamelide in these experiments proves that cyanic acid was liberated in the enol-form, since the generation of this polymeride takes effect from the change HOCN $\longrightarrow$ HNCO. When a solution of ammonia in pure ether at $-8°$ was gradually added to a similar solution of cyanic acid, the crystalline product which immediately separated was found to be a mixture of ammonium cyanate and urea in the proportion of 6 to 2·6 respectively.

Note on the Xanthhydrol Test for Urea.

The use of xanthhydrol for the detection and estimation of urea depends on the formation of a very sparingly soluble condensation product. Fosse (*Compt. rend.*, 1907, **145**, 813; 1913, **156**, 1938) recommends pure acetic acid as the solvent in applying the test. This introduces certain limitations, and where the detection of a

* For this reason, 75 minutes must be taken as the limit up to which the change had proceeded undisturbed in accordance with the primary reactions.

trace of urea in a relatively large volume of water is desired, the process is tedious.

As a matter of fact, xanthhydrol is not a test for "free" urea; thus, in alcoholic solution, no reaction was effected, even after heating at 100° in a sealed tube for several days. After the addition of one drop of concentrated hydrochloric acid, the condensation product was precipitated, and its formation was completed within ten minutes. The solubility of dixanthylurea in pure alcohol at 15° was equal to 0·009 gram in 100 c.c.

A salt of urea must be formed in order to bring about the necessary configuration of the urea molecule before it can react with xanthhydrol, and, in accordance with this view, the test can be applied as follows.

A saturated aqueous solution of xanthhydrol (containing 0·13 gram in 1000 c.c. at 15°) is readily prepared by adding the reagent, previously dissolved in 2 c.c. of alcohol, to a litre of boiling water. The cold solution (filtered, if necessary), when added in considerable excess (not less than 6 vols. to 1) to an aqueous solution containing urea to which a few drops of hydrochloric acid have been added, will reveal 1 part in 10,000 within fifteen seconds, whilst 1 part of urea in 800,000 can be detected in about ten minutes.

The solution of xanthhydrol loses its sensitiveness after about a week, on account of gradual oxidation to xanthone.

EXPERIMENTAL.

I. *Polymerisation of Cyanic Acid.*—The results given in table I were obtained as follows: cyanic acid was prepared from pure, dry cyanuric acid, which was heated electrically in a hard glass tube so arranged that the heating could be continued right up to the neck of the receiver. The construction of the latter was such that liquid cyanic acid collected in the narrow space between an inner and an outer vessel, each of which was kept at 0°. A relatively large surface of the acid was thus maintained at a constant temperature, and by careful avoidance of agitation, which was found to be a great promoter of the change, polymerisation was allowed to proceed as slowly as possible. The ice in the outer vessel only was displaced by water at the temperature at which it was desired to bring about polymerisation; in this way only was it possible to control, within reasonable limits, the temperature at which the change took effect.

A weighed quantity of the polymeride was extracted with hot water; the cyanuric acid present was estimated by titration with $N/10$-sodium hydroxide, using phenolphthalein as indicator.

Whilst it was necessary to prepare small portions of cyanic acid for each experiment, the values given represent the mean of many more experiments than are recorded.

II. *Formation of Urea at* 0°.—Cyanic acid was estimated by precipitation with an excess of silver nitrate, and the silver cyanate, dissolved in dilute nitric acid, was titrated by Volhard's method. The filtrate, freed from the excess of silver, was rendered just alkaline by addition of pure lime, and, after the removal of all traces of ammonia, urea was estimated in the residue by (*a*) the "hypobromite" method, (*b*) decomposition by urease, and (*c*) precipitation with xanthhydrol. The presence of biuret was proved by the copper test.

Part of the expense of this research was defrayed by the Mackinnon Research Studentship of the Royal Society granted to one of us (W.R.F.).

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CXLVIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part I. Some Derivatives of* cyclo*Pentene and* dicyclo*Pentane.*

By ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD.

PERKIN and Thorpe (T., 1901, **79**, 729) showed that when ethyl $\alpha\alpha'$-dibromo-$\beta\beta$-dimethylglutarate is condensed with ethyl malonate in the presence of an excess of sodium ethoxide there is formed a remarkable yellow sodium compound, to which hitherto the formula I has been ascribed. Numerous derivatives of this substance were prepared both by hydrolysis and by alkylation and subsequent hydrolysis, and many of the products so obtained were subjected to oxidation and reduction. Much more recently, one of us, in conjunction with Prof. J. F. Thorpe, prepared from ethyl $\alpha\alpha'$-dibromo*cyclo*hexane-1:1-diacetate a second, rather similar yellow sodium compound (II). This also yielded a large number

$$CMe_2<\begin{array}{l}C(CO_2Et)\cdot C{:}C(ONa)\cdot OEt\\ C(CO_2Et)\cdot CO\end{array}$$

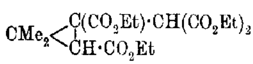
(I.)

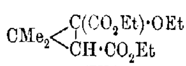
$$CH_2<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}>C<\begin{array}{l}C(CO_2Et)\cdot C{:}C(ONa)\cdot OEt\\ C(CO_2Et)\cdot CO\end{array}$$

(II.)

of hydrolytic products analogous, broadly speaking, to those of the *gem*-dimethyl series, but exhibiting a number of very striking differences, which were studied in some detail (T., 1919, **115**, 320) and correlated in a definite manner to the constitutions of the substances concerned.

In the course of neither of these investigations has there been discovered any fact which could reasonably be regarded as casting doubt on the bridged structures assigned to these sodium compounds and to their more immediate derivatives. On the contrary, much evidence confirming these structures has been accumulated. The principal item consists, of course, in the mode of formation of the sodium compounds. Thus, when ethyl $\alpha\alpha'$-dibromo-$\beta\beta$-dimethylglutarate is treated with two molecular proportions of ethyl sodiomalonate, there is formed the sodium compound of an ester, which, as it can readily be alkylated, cannot but have the structure III. This structure is quite inevitable, and is strictly analogous to that of ethyl ethoxycaronate (IV), which is formed by the action of sodium ethoxide on the dibromo-ester. The ester (III), on being treated with sodium in xylene, or with an excess of alcoholic sodium ethoxide, loses one molecule of ethyl alcohol, and is converted into the yellow sodium compound, which therefore must have either formula I or formula V. Of these, the former alone is capable of


(III.)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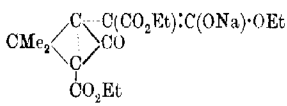
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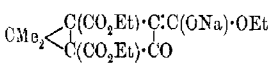
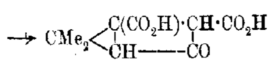
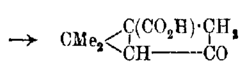
interpreting the many decompositions of the substance.

Quite recently, doubt has been cast by Toivonen (*Annalen*, 1919, **419**, 176) on the bridged constitution which has hitherto been assigned to these compounds. When the sodium compound (I) is hydrolysed by acids, it yields, first, a dibasic acid (VI), and, finally, a monobasic acid (VII). This monobasic acid was obtained by


(I.)


(VI.)


(VII.)

3 D* 2

Toivonen in the course of some experiments on the oxidation of *iso*dehydrofenchoic acid, and, as a result of his investigations, he formed the opinion that, not only this acid, but all the compounds of the series, including the yellow sodium compound itself, were unsaturated substances containing the *cyclo*pentene, and not the *dicyclo*pentane, ring system. Thus, according to Toivonen, the sodium compound would be represented by the formula VIII, the dibasic acid by IX, and the monobasic acid by X. Toivonen found

$$\underset{\text{(VIII.)}}{CMe_2\Big<\begin{array}{l}C(CO_2Et)\!=\!=\!=\!=C\cdot CO_2Et\\ C[:C(ONa)\cdot OEt]\cdot CO\end{array}} \longrightarrow \underset{\text{(IX.)}}{CMe_2\Big<\begin{array}{l}C(CO_2H)\!=\!CH\\ CH(CO_2H)\cdot CO\end{array}} \longrightarrow$$

$$\underset{\text{(X.)}}{CMe_2\Big<\begin{array}{l}C(CO_2H)\!:\!CH\\ CH_2\!-\!-\!-\!-CO\end{array}}$$

that the oxidation of *iso*dehydrofenchoic acid by alkaline permanganate proceeded in two stages. In the first place, a diketonic acid (XI) was produced. This then underwent internal condensation under the influence of the alkali, and gave Perkin and Thorpe's acid, with the elimination of one molecule of water. Toivonen represents this reaction as follows:

$$\underset{\text{(XI.)}}{CMe_2\Big<\begin{array}{l}CO\cdot CO_2H\\ CH_2\cdot CO\cdot CH_3\end{array}} \longrightarrow \underset{\text{(X.)}}{CMe_2\Big<\begin{array}{l}C(CO_2H)\!:\!CH\\ CH_2\!-\!-\!-\!-CO\end{array}} + H_2O$$

We therefore have two methods of formation of one and the same substance which are exceedingly difficult to reconcile with one another. In fact, one must either assume that the conversion of the ester (III) into the yellow sodium compound, instead of being a simple Dieckmann condensation, is a remarkable change involving the rupture by alcoholysis of the *cyclo*propane ring, possibly as in the following scheme:

$$CMe_2\Big<\begin{array}{l}C(CO_2Et)\cdot CH(CO_2Et)_2\\ CH\cdot CO_2Et\end{array} \longrightarrow CMe_2\Big<\begin{array}{l}C(CO_2Et)(OEt)\cdot CH(CO_2Et)_2\\ CH_2\cdot CO_2Et\end{array}$$

$$\longrightarrow CMe_2\Big<\begin{array}{l}C(CO_2Et)(OEt)\cdot CH\cdot CO_2Et\\ CH(CO_2Et)\!-\!-\!-CO\end{array} \longrightarrow$$

$$CMe_2\Big<\begin{array}{l}C(CO_2Et)\!=\!C\cdot CO_2Et\\ CH(CO_2Et)\cdot CO\end{array}$$

or regard the internal condensation of dimethyldiketohexoic acid (XI) as taking place in two stages. In the first place, there must

be formed a cyclic aldol condensation product (XII), which is then dehydrated across the *cyclo*pentane ring:

$$\mathrm{CMe_2}\!<\!\begin{array}{l}\mathrm{CO{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO{\cdot}CH_3}\end{array} \longrightarrow \mathrm{CMe_2}\!<\!\begin{array}{l}\mathrm{C(OH)(CO_2H){\cdot}CH_2}\\ \mathrm{CH_2}\text{———————}\mathrm{CO}\end{array} \longrightarrow$$
$$\text{(XI.)} \qquad\qquad\qquad \text{(XII.)}$$

$$\mathrm{CMe_2}\!<\!\begin{array}{l}\mathrm{C(CO_2H){\cdot}CH_2}\\ \mathrm{CH}\text{————}\mathrm{CO}\end{array}$$
$$\text{(VII.)}$$

Both alternatives appear almost equally extraordinary.

The subject therefore obviously required fresh investigation, and some months ago we were asked by Prof. J. F. Thorpe to undertake this work, and there have now been obtained results which show unquestionably that, for the series of compounds with which we are here concerned, the bridged, and not the unsaturated, constitution is correct.

Turning, first, to the facts which have already been placed on record, one observes two reasons why the formulæ suggested by Toivonen cannot be regarded as adequate. The first concerns the dibasic acid, the bridged formula for which is VI, the double-bonded formula IX. That the alternative formulæ, XIII and

$$\mathrm{CMe_2}\!<\!\begin{array}{l}\mathrm{C(CO_2H){\cdot}CH_2}\\ \mathrm{C(CO_2H){\cdot}CO}\end{array} \qquad\qquad \mathrm{CMe_2}\!<\!\begin{array}{l}\mathrm{C(CO_2H){:}C{\cdot}CO_2H}\\ \mathrm{CH_2}\text{———}\mathrm{CO}\end{array}$$
$$\text{(XIII.)} \qquad\qquad\qquad \text{(XIV.)}$$

XIV, are incorrect is proved by the fact that the acid is a tautomeric substance; it readily gives a coloration with ferric chloride, and its ester can be alkylated. Now an acid of the formula IX, in which, as an examination of structural models shows, the carboxyl groups are actually further apart than is the case with such compounds as *trans*-hexahydro*iso*phthalic acid or *cis*-hexahydroterephthalic acid, would not be expected to form an anhydride. Actually, however, the acid does form an anhydride with the greatest of ease, a fact which is in full accordance with the bridged-ring formula (VI).

The second point arises in connexion with the ester produced by methylating the yellow sodium compound with methyl iodide. The bridged and unsaturated structures for this substance are shown in formulæ XV and XVI. On treating with alcoholic potassium hydroxide, there is formed the lactone of a hydroxy-tribasic acid, the production of which involves (*a*) the hydrolysis of all three carbethoxyl groups to carboxyl; (*b*) the loss of one carboxyl group by elimination of carbon dioxide; (*c*) fission, with the addition of water in the immediate neighbourhood of the

ketone group, which thus becomes a carboxyl group; (*d*) a further fission, with the addition of water. Now, whether formula XV

$$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{C(CO_2Et)\cdot CMe\cdot CO_2Et}\\ \mathrm{C(CO_2Et)\cdot CO}\end{matrix} \qquad \mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{C(CO_2Et){=\!=}C\cdot CO_2Et}\\ \mathrm{CMe(CO_2Et)\cdot CO}\end{matrix}$$

(XV.) (XVI.)

or formula XVI is adopted, process (*a*) can only take place in one way, process (*b*) in two ways, and process (*c*) in two ways. If one adopts the structure XV, the addition of a further molecule of water, process (*d*), must involve the fission of one of the *cyclo*-propane bonds. This could take place in six ways. On the other hand, if formula XVI be accepted, the addition must take place at the double bond, since the product is fully saturated. This might occur in two ways. On considering the combinations of these possibilities, one observes that, as many lead to the same formulæ, there are but six possible structures for such a hydroxy-tribasic acid derived from an ester of the constitution XV, and six from an unsaturated ester of the constitution XVI. The properties of the lactone (*loc. cit.*) show, however, that in the corresponding hydroxy-acid, (*a*) the hydroxyl group is in the γ-position with respect to one of the three carboxyl groups; (*b*) that no two carboxyl groups are attached to the same carbon atom; (*c*) that the two carboxyl groups, other than that to which the hydroxyl group is in the γ-position, are attached to two carbon atoms directly united. These conditions reduce the number of possible formulæ derived from the structure XV to three, one of which is the accepted one, and the number from XVI to one only, namely, XVII. It will be seen that this differs from the customary formula

$$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{C(CO_2H)\cdot CH_2\cdot CO_2H}\\ \mathrm{CHMe\cdot CO\cdot O}\end{matrix} \qquad \mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{C(CO_2H)\cdot CHMe\cdot CO_2H}\\ \mathrm{CH_2\cdot CO\cdot O}\end{matrix}$$

(XVII.) (XVIII.)

(XVIII) only in the position of the single methyl group. The difference, however, is an important one, as the lactonic acid was found to exist in two forms, namely, a *cis*- and a *trans*-form (or meso- and racemic), each of which yields its own anhydride, that of the *trans*-lactonic acid passing on distillation into that of the *cis*-lactonic acid. This property is characteristic of substances of the type of *s*-dimethylsuccinic acid, and clearly proves that there exists in the molecule of the lactonic acid a free, open-chain succinic acid residue in which both the carboxyl-bearing carbon atoms are asymmetric. This condition is fulfilled by formula XVIII, but formula XVII is obviously incorrect, as it lacks one of the necessary asymmetric carbon atoms in the succinic acid group. One must

therefore conclude that the unsaturated structure XVI for the methylation product of the yellow sodium compound is incapable of interpreting the properties of the products obtained by hydrolysis.

Toivonen, however, was more deeply impressed with the behaviour of the monobasic acid on oxidation. Perkin and Thorpe had shown (*loc. cit.*) that, when treated with alkaline permanganate, it was converted into $\alpha\alpha$-dihydroxy-$\beta\beta$-dimethylglutaric acid (XXII). Toivonen proved that the reaction could be carried out at the ordinary temperatures, and, as it is capable of being easily explained along conventional lines if the unsaturated structure be assumed, he saw in it conclusive confirmation of this method of formulation. The successive stages are as follows:

$$\underset{\text{(X.)}}{CMe_2<\begin{matrix}C(CO_2H){:}CH\\CH_2\text{———}CO\end{matrix}} \rightarrow \underset{\text{(XIX.)}}{CMe_2<\begin{matrix}(CO_2H)(OH)\cdot CH\cdot OH\\CH_2\text{————}CO\end{matrix}} \rightarrow$$

$$\underset{\text{(XX.)}}{CMe_2<\begin{matrix}C(OH)_2\cdot CO_2H\\CH_2\cdot CO\cdot CHO\end{matrix}} \rightarrow \underset{\text{(XXI.)}}{CMe_2<\begin{matrix}C(OH)_2\cdot CO_2H\\CH_2\cdot CO\cdot CO_2H\end{matrix}} \rightarrow$$

$$\underset{\text{(XXII.)}}{CMe_2<\begin{matrix}C(OH)_2\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}} \rightarrow \underset{\text{(XXIII.)}}{CMe_2<\begin{matrix}CO_2H\\CH_2\cdot CO_2H\end{matrix}}$$

In practice, between four and five atoms of oxygen are taken up, and the product is a mixture of dihydroxydimethylglutaric acid (XXII) and *as*-dimethylsuccinic acid (XXIII).

In spite of the apparent simplicity of this explanation, the issue is not, in reality, quite so clear. For, as was shown in the paper by Ingold and Thorpe (*loc. cit.*), the bridge-bond in such *dicyclo*pentane systems is in a condition of great strain, and may become —in fact, in certain circumstances it undoubtedly does become—the most unstable part of the molecule, giving rise to reactions the similarity of which with the reactions characteristic of unsaturated compounds is very striking. This state of strain owes its origin to the fact that, in both the rings to which the bridge-bond is common, the internal angles are considerably less than the normal angle at which two free valencies are inclined (Ingold and Thorpe, *loc. cit.*). The case of carone is very different. Here the internal angles between the valencies in the two rings separated by the bridge differ in opposite ways from the normal angle of inclination of carbon valencies. There is, therefore, a mutual accommodation existing between the strains which react on the carbon atoms terminating the bridge, rendering the latter stable to a considerable degree. The theory of the matter may readily be placed on

a quantitative basis by a simple calculation on lines indicated elsewhere (*loc. cit.*; note, this vol., p. 603). Therefore Toivonen's argument that, because carone, dimethyl*dicyclo*heptanone (XXXI, p. 1370), can be oxidised by permanganate to a *cyclo*propane derivative, namely, caronic acid (XXXII, p. 1370), the acids derived from dimethyl*dicyclo*pentanone should behave similarly with this reagent, cannot be regarded as being in the least degree convincing. On a priori grounds, it might be very difficult to discover an oxidising agent capable of attacking the four-membered ring at the carbonyl group, and yet leaving the somewhat unstable bridge-bond intact. On the other hand, should such a substance as caronic acid be obtainable by oxidation under special and carefully regulated conditions, the circumstance could not but be regarded as the clearest possible proof of the dicyclic constitution of this series of compounds. This proof we have now been able to supply.

The general plan pursued in our experiments was as follows. If the alternative formulæ VI and IX for the dibasic acid, and the two formulæ XV and XVI for the methylation product of the yellow sodium compound, be examined, it will be noticed that in the one case a carboxyl group, and in the other a methyl group, is in a different position relative to the *gem*-dimethyl group in the two alternative formulæ. It should be possible to ascertain the true positions of these groups by oxidation. Thus, for example, whilst the ester (XV), after hydrolysis and oxidation, might perhaps yield some derivative of $\beta\beta$-dimethylglutaric acid, an ester the formula of which is XVI should give derivatives, not of $\beta\beta$-dimethylglutaric acid, but of $\alpha\beta\beta$-trimethylglutaric acid. There are similar differences in the oxidation products to be expected from dibasic acids having the structures VI and IX. A number of interesting results have already been obtained in this field, but it has become apparent that an extended investigation is necessary both in the series with which we are here concerned and in other related ones. It is therefore our desire to place on record at the present time only a limited number of experiments on the oxidation of the dibasic acid (VI), which, however, supply singularly convincing evidence regarding its structure.

In the first place, when an aqueous solution of the dibasic acid is titrated with cold alkaline permanganate, a sharp end-point is reached after three atoms of available oxygen have been taken up. The resulting solution contains $\alpha\alpha$-dihydroxy-$\beta\beta$-dimethylglutaric acid and oxalic acid, the reaction

$$C_9H_{10}O_5 + 3O + 2H_2O = C_7H_{12}O_6 + C_2H_2O_4$$

being apparently quantitative. The behaviour of the dibasic acid

with permanganate is therefore very similar to that of the monobasic acid (VII). The remarkable fact regarding the production of this dihydroxydimethylglutaric acid by the action of cold alkaline permanganate on these acids is that the fission of the bridge-bond is not due to oxidation, but is of a purely hydrolytic character. There is therefore no analogy to fission of the double bond in unsaturated substances by permanganate, the first stage of which involves the addition of two hydroxyl groups. The fission of the bridge must be assumed to be due to the addition, not of 2OH, but of H·OH, otherwise it is not possible to account for the structure of the product. The oxidation, for example, of the dibasic acid is therefore to be represented as follows:

$$\underset{\text{(VI.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(CO_2H)\cdot CH\cdot CO_2H} \\ \mathrm{CH\text{------}CO}\end{matrix}} \rightarrow \underset{\text{(XXIV.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(CO_2H)(OH)\cdot CH\cdot CO_2H} \\ \mathrm{CH_2\text{---------}CO}\end{matrix}}$$

$$\rightarrow \underset{\text{(XXV.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH_2\cdot CO\cdot CH(OH)\cdot CO_2H}\end{matrix}} \rightarrow \underset{\text{(XXVI.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH_2\cdot CO\cdot CO\cdot CO_2H}\end{matrix}}$$

$$\rightarrow \underset{\text{(XXII.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH_2\cdot CO_2H}\end{matrix}} + \mathrm{CO_2H\cdot CO_2H}$$

If the process is conducted with care, no dimethylsuccinic acid is formed. A precisely analogous scheme, involving an intermediate hydrolytic product similar to XXIV, and two intermediate oxidation products, like XXV and XXVI, may be considered as representing the course of the oxidation of the monobasic acid—only in this case four atoms of oxygen are taken up, as the final product, which replaces oxalic acid in the scheme outlined above, is not formic acid, but carbon dioxide.

The formation of oxalic acid along with dihydroxydimethylglutaric acid when the dibasic acid is oxidised affords an interesting confirmation of the existence originally of the bridged structure. For, if the double-bonded formula IX for the original acid were correct, the production of oxalic acid as a main product would be impossible. Four, and not three, atoms of oxygen would be taken up, the successive changes being represented as follows:

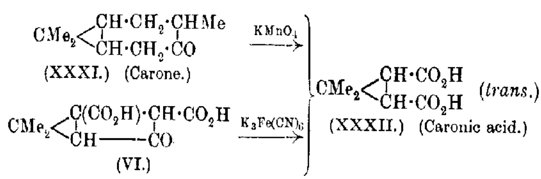
$$\underset{\text{(IX.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(CO_2H)\!=\!CH} \\ \mathrm{CH(CO_2H)\cdot CO}\end{matrix}} \rightarrow \underset{\text{(XXVII.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)(CO_2H)\cdot CH\cdot OH} \\ \mathrm{CH(CO_2H)\text{----}CO}\end{matrix}} \rightarrow$$

$$\underset{\text{(XXVIII.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH(CO_2H)\cdot CO\cdot CHO}\end{matrix}} \rightarrow \underset{\text{(XXIX.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH(CO_2H)\cdot CO\cdot CO_2H}\end{matrix}} \rightarrow$$

$$\underset{\text{(XXX.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH(CO_2H)_2}\end{matrix}} \rightarrow \underset{\text{(XXII.)}}{\mathrm{CMe_2}<\begin{matrix}\mathrm{C(OH)_2\cdot CO_2H} \\ \mathrm{CH_2\cdot CO_2H}\end{matrix}}$$

In this method of representation, the intermediate products XXVII to XXX are strictly analogous to the substances XIX to XXII which figure in the corresponding scheme (p. 1367) for the oxidation of the monobasic acid, whilst the direct elimination of a carboxyl group as carbon dioxide from the acid XXX appears to be the only method of accounting for the unsubstituted methylene group in the final product. We are unable to see any plausible alternative mechanism whereby the formation of oxalic acid along with dihydroxydimethylglutaric acid by the oxidation of an unsaturated substance having the formula IX might be explained.

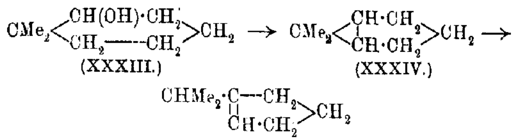
Owing to the curious hydrolytic action on the bridge-bond to which reference has just been made, it does not appear possible to obtain *cyclo*propane derivatives by oxidation with permanganate. We have experimented with many other oxidising agents under a variety of conditions, and have discovered two reagents by means of which it is possible to produce caronic acid from the dibasic acid, which therefore must have the bridged structure VI. These are hydrogen peroxide and potassium ferricyanide. In the former case, the conditions necessary in order to obtain a good yield of caronic acid appear rather difficult to determine, but with cold ferricyanide the oxidation proceeds very smoothly, and, if a little of the reagent is added each day, is complete in rather more than a week, when an excellent yield of *trans*-caronic acid can be extracted from the solution. The direct comparison with the case of carone asked for by Toivonen now becomes possible:



(XXXI.) (Carone.) (VI.) (XXXII.) (Caronic acid.)

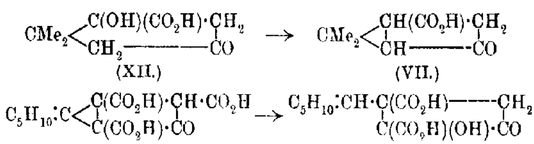
If this experiment places, as we believe it does, the bridged constitution beyond doubt, there appears to be no alternative to accepting the mechanism proposed on p. 1365 for the internal condensation of Toivonen's dimethyldiketohexoic acid (XI). Such a reaction is not, however, entirely without precedent, for the intermediate aldol-condensation product (XII) is a cyclic pinacoline alcohol very similar in constitution to the dimethyl*cyclo*hexanol (XXXIII), the dehydration of which has been investigated by Meerwein (*Annalen*, 1914, **405**, 129), who found it to take place across the ring, the final product being *iso*propyl*cyclo*-

pentene (XXXV). We assume that intermediately a bridged compound (XXXIV) is formed:



(XXXIII.) (XXXIV.) (XXXV.)

The difference between this case and that with which we are concerned lies in the fact that the hydroxy-compound (XII), owing presumably to the presence of the ketone and carboxyl groups, undergoes dehydration spontaneously, or at any rate under very mild conditions. For the same reason, the reaction stops at the first stage: the presence of the carboxyl group makes the analogous isomerisation impossible. Although no reaction resembling this isomeric change has been observed amongst the derivatives of *gem*-dimethyl*dicyclo*pentane, there has been noticed (Ingold and Thorpe, *loc. cit.*) in the *cyclo*hexane*spirodicyclo*pentane series a hydrolytic decomposition showing a considerable degree of similarity. The connexion is best exhibited by means of the formulæ expressed below, and from these it will be seen that both stages of the above scheme for the dehydration of dimethyl*cyclo*hexanol have their counterpart. The *cyclo*hexyl*cyclo*butanolone acid (XXXVII) is obviously incapable of eliminating the elements of water and passing into a *cyclo*butene derivative as the strict analogy requires.



(XII.) (VII.) (XXXVI.) (XXXVII.)

The above considerations have an obvious implication regarding the internal condensation of other diketones, and it is hoped in the future to devote attention to this and similar questions.

EXPERIMENTAL.

*Oxidation of Dimethyl*dicyclo*pentanonedicarboxylic Acid* (VI, p. 1363) *by Cold Alkaline Permanganate: Formation of* ***αα-Dihydroxy-ββ-dimethylglutaric Acid and Oxalic Acid.***

Two grams of the *dicyclo*pentanone acid were dissolved in a small excess of aqueous potassium carbonate and carefully titrated

in the cold with a 3 per cent. solution of potassium permanganate. When three atoms of oxygen had been taken up, the permanganate ceased to be decolorised. The solution was then treated with a current of steam and filtered, the precipitate of manganese dioxide being extracted with boiling water. The combined filtrates were acidified with hydrochloric acid, boiled for a few minutes, and then rendered alkaline with ammonia. On adding calcium chloride to this solution, there was obtained a precipitate of calcium oxalate, which was collected and washed with dilute acetic acid in order to remove any traces of admixed calcium carbonate. The filtrate from the calcium oxalate was evaporated to a small bulk, acidified with hydrochloric acid, and exhaustively extracted with pure ether. On drying and evaporating the extract, there was obtained a nearly quantitative yield of αα-dihydroxy-ββ-dimethylglutaric acid. The acid prepared in this way melted at 83—84°, and after recrystallisation from chloroform at 84° (Found: C=44·20; H=6·37. Calc.: C=43·7; H=6·3 per cent.).

Further proof of the identity of the acid was obtained by means of a direct comparison with a specimen prepared from the hydrogen ester of αα-dibromo-ββ-dimethylglutaric acid (Perkin and Thorpe, *loc. cit.*, p. 757). Both preparations, as well as a mixture of the two, melted at 84°.

αα-Dihydroxy-ββ-dimethylglutaric acid may also be obtained from the *dicyclo*pentanone acid by oxidation with sodium manganate.

*Oxidation of Dimethyl*dicyclo*pentanonedicarboxylic Acid* (VI, p. 1363) *by Cold Ferricyanide: Formation of* trans-*Caronic Acid.*

Thirty-three grams of potassium ferricyanide and 8 grams of potassium carbonate were dissolved in 140 c.c. of water, and one-fifth of this solution was added daily to 2 grams of the *dicyclo*pentanone acid dissolved in a slight excess of aqueous potassium carbonate. After the addition of the reagent was finished, the mixture was allowed to remain for another period of five days, and was then acidified and extracted repeatedly with pure ether. On drying and evaporating the ether, there remained a crystalline residue, which, after washing with chloroform and recrystallising from water, melted at 213° [Found: C=53·13; H=6·41. Calc.: C=53·1; H=6·4 per cent. 0·0435 required 40·7 c.c. of 0·0135*N*-$Br(OH)_2$. $C_5H_8(CO_2H)_2$ requires 40·8 c.c.].

There can be no doubt that this substance is *trans*-caronic acid. It was identified with a known specimen of this acid by direct

comparison and by the method of mixed melting point. In addition, it was converted by means of hydrobromic acid and by hydrochloric acid into terebic acid, which was similarry identified by comparison with a known specimen and by a mixed melting-point determination. Before we were aware that the product of this oxidation was *trans*-caronic acid, we recrystallised the crude residue from the ether from concentrated hydrochloric acid. This treatment caused a considerable degree of conversion into terebic acid. Consequently, after several recrystallisations we obtained pure terebic acid apparently as the sole crystalline oxidation product. The extraordinary ease with which this reaction takes place does not appear to have been noticed previously (compare Beasley, Ingold, and Thorpe, T., 1915, **107**, 1080).

A search for *cis*-caronic acid amongst the residues of the oxidation proved fruitless.

trans-Caronic acid may also be obtained by oxidising the original acid with cold alkaline hydrogen peroxide.

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CXLIX.—*A New Type of Compound containing Arsenic.*

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

HITHERTO, our knowledge of additive compounds formed from arsines has been restricted to those of the cacodyl series, and the compounds in question are of the co-ordination type and contain such elements as platinum, mercury, and copper. The authors have found that many arsines of the type $R_1R_2R_3As$, where R_1, R_2, and R_3 may be similar or dissimilar alkyl or aryl groups, combine readily with methyldi-iodoarsine and with the corresponding ethyl and phenyl derivatives to give brightly-coloured substances varying in shade from pale yellow to deep orange, and of the general type $R_1R_2R_3As,RAsI_2$. They are completely dissociated into their parent substances on dissolving in benzene, but evaporation of such solutions gives the pure additive compound

once more. They react in benzene solution with methyl iodide, with precipitation of the methiodide of the arsine, the alkyl- or aryl-di-iodoarsine remaining in solution. The solid additive compounds cannot be said to be unstable, remaining unchanged indefinitely under ordinary conditions, but they crystallise only with difficulty from some solvents, apparently owing to the retarding influence of the latter on the rate of addition of the two substances, giving rise to the additive compound.

The authors hesitate, without further experimental work, to suggest definite formulæ for the additive compounds. These may evidently be simple "molecular compounds" or compounds analogous to those formed between arsines and methylene iodide, and of the type $R_1R_2R_3IAs{\cdot}AsRI$.

In support of this structure can be cited the fact that, as a rule, an additive compound is paler than the di-iodoarsine from which it is formed, and the further fact that iodine attached to arsenic in the quinquevalent condition has no chromophoric properties. Against the structure given above, however, is the fact of ready dissociation in benzene solution.

Phenyldimethylarsine, phenylmethylethylarsine, and phenyldiethylarsine, in their behaviour towards di-iodoarsines, illustrate well the subject under discussion, and the melting points of the various substances involved are tabulated below:

	$MeAsI_2$ (30°).	$PhAsI_2$ (15°).	EtAsI (−9°).
$PhMe_2As$ (liquid)	94°	69°	44°
PhMeEtAs (liquid)	84	55°	—
$PhEt_2As$ (liquid)	79	—	—

In each of the nine cases allowed for by this table, combination undoubtedly occurred, since, on mixing the pair of substances in question, heat was evolved. Only six compounds were actually isolated, and from the melting-point regularities this fact can no doubt be attributed to the low melting points of the three compounds which could not be isolated. Attention should perhaps be drawn to the isomerism of the additive compounds

$$PhMeEtAs,MeAsI_2 \text{ and } PhMe_2As,EtAsI_2.$$

On the other hand, certain arsines show no tendency to form additive compounds with di-iodoarsines, no heat being evolved on mixing the substances in question. Thus, diphenylmethylarsine, triphenylarsine, and other aromatic arsines could not be caused to combine with di-iodoarsines under a wide range of experimental conditions.

Phenyldichloroarsine has also been found to form an additive compound with the most reactive of the arsines in our possession,

namely, phenyldimethylarsine. The compound is strictly analogous to the iodo-compounds just described, and the effect of heat on chloro-additive compounds generally, if they can be prepared, will be investigated, since some light might thus be thrown on the interaction between, say, triphenylarsine and arsenious chloride, which proceeds in a very irregular manner and is greatly influenced by temperature (compare Michaelis and Loesner, *Ber.*, 1891, **27**, 294, etc.).

The iodo-derivatives of arsenic have been found to be the most suitable for the preparation of the various types of arsines. They react almost quantitatively with Grignard reagents, giving the expected arsines in all cases so far studied. The use of arsenious chloride or bromide (Auger and Billy, *Compt. rend.*, 1904, **139**, 597; Hibbert, *Ber.*, 1906, **39**, 160) is to be avoided, as very low temperatures are necessarily involved.

EXPERIMENTAL.

Methyldi-iodoarsine.

This substance was prepared by Auger's method (*Compt. rend.*, 1906, **142**, 1151), and was purified by distillation under diminished pressure. It boiled without decomposition at 128°/16 mm., and gave, on cooling, a bright yellow solid melting at 30° (Auger, *loc. cit.*, gives 25°). On one occasion, 320 grams of arsenious oxide, converted into sodium methylarsinate by the method described by Klinger and Kreutz (*Annalen*, 1888, **249**, 149), gave more than 500 grams of pure, redistilled methyldi-iodoarsine (Found: M.W. [by cryoscopic method in benzene] = 331, 340. Calc.: M.W. = 344).

In view of certain results obtained in other directions, it is considered possible that in other solvents methyldi-iodoarsine may be associated, although at present no direct evidence can be put forward in connexion with this point. The ease with which methyldi-iodoarsine may be prepared renders this substance a very convenient starting material for the preparation of arsenic derivatives. In this connexion, it is of interest to note that whereas methyl iodide reacts almost quantitatively in the course of a few hours with sodium arsenite in aqueous-alcoholic solution, ethyl iodide reacts much more slowly, a 57 per cent. conversion of sodium arsenite into ethyldi-iodoarsine (see below) being the maximum so far obtained.

Ethyldi-iodoarsine.

The product obtained (compare McKenzie and Wood, this vol., p. 408) by the reduction of ethylarsinic acid was dried over

calcium chloride, and the sulphur dioxide present removed by gentle warming under diminished pressure, the whole of the liquid finally being distilled under the same conditions. Ethyldi-iodo-arsine was obtained in this way as a reddish-yellow oil boiling at 126°/11 mm., and setting to a pale yellow, crystalline solid (m. p. −9°) on cooling in solid carbon dioxide.

Phenyldi-iodoarsine.

A mixture of phenyldichloroarsine (34 grams), 90 grams (a large excess) of finely powdered sodium iodide, and 100 c.c. of absolute alcohol was shaken for three hours in the cold, filtered, and the filtrate evaporated to dryness under diminished pressure. The residue was extracted with chloroform, and the filtered extract evaporated under diminished pressure until quite free from chloroform. A brownish-red oil, in amount corresponding with an almost theoretical conversion of dichloro- into di-iodo-arsine, was obtained, and was purified by crystallisation from alcohol, using solid carbon dioxide as an external refrigerant. In this way, pure phenyldi-iodoarsine was obtained in lemon-yellow clusters of needles melting (after remaining in contact with porous porcelain at a low temperature) at 15° (Found: I=62·9.* M.W. [by cryoscopic method in benzene]=393, 401. $C_6H_5I_2As$ requires I=62·6 per cent. M.W.=406).

Phenyldi-iodoarsine resembles the corresponding methyl and ethyl derivatives in odour and physiological properties. It undergoes slight decomposition when distilled under diminished pressure, boiling at 190°/12 mm. The effect of heat on the product obtained by Michaelis and Schulte (*Ber.*, 1881, **14**, 913), by the action of hydriodic acid on phenylarsenious oxide, shows that this product was, even before heating, a mixture of several substances.

Dimethyliodoarsine.

The difficulty of obtaining derivatives of cacodyl has now been removed by the discovery that Auger's method for the reduction of methylarsinic acid to methyldi-iodoarsine (*loc. cit.*) may be applied to the conversion of dimethylarsinic (cacodylic) acid into dimethyliodoarsine (cacodyl iodide).

A solution of 250 grams of cacodylic acid and 800 grams of potassium iodide in 1 litre of water was saturated with sulphur dioxide, dilute hydrochloric acid (500 c.c. of concentrated acid and

* All these compounds in which iodine and arsenic are directly combined (whether the arsenic be ter- or quinque-valent) react quantitatively with silver nitrate in alcoholic solution.

500 c.c. of water) being added from time to time. Reduction proceeded rapidly, with the separation of dimethyliodoarsine as a yellow oil, the end of the process being indicated by the separation also of sulphur. The oily layer was separated, dried over calcium chloride, and distilled, when pure dimethyliodoarsine (380 grams, corresponding with a 90 per cent. conversion) was obtained as a yellow liquid boiling at 154—157°, and freezing to a pale yellow, crystalline solid at about $-35°$.

From dimethyliodoarsine, cacodyl oxide, chloride, etc., may readily be prepared, without the production of intermediate compounds, which are spontaneously inflammable.

Phenylmethyliodoarsine and Phenylmethylchloroarsine.

By a similar reduction process, phenylmethylarsinic acid (Bertheim, *Ber.*, 1915, **48**, 350) has been converted into phenylmethyliodoarsine.

The phenylarsenious oxide required was prepared by treating phenyldichloroarsine with excess of powdered sodium hydrogen sulphite in the presence of a little water. On removing the inorganic matter by repeated extraction with hot water, the pure oxide was left behind, and, when cold, could be ground up, and was then used without further purification for conversion into phenylmethyliodoarsine.

Phenylarsenious oxide (50 grams) was dissolved in a solution of 30 grams of sodium hydroxide in 240 c.c. of rectified spirit and 60 c.c. of water, the solution cooled, and treated with 30 c.c. of methyl iodide. A vigorous reaction set in, and was allowed to complete itself overnight. The mixture was acidified, freed from alcohol by distillation, treated with 50 grams of potassium iodide, and saturated with sulphur dioxide. The dark oil formed was separated, dried over calcium chloride, and distilled, when 54 grams of phenylmethyliodoarsine, a yellow oil boiling at 138—140°/12 mm., were obtained (Found: I=43·7. C_7H_8IAs requires I=43·2 per cent.).

It is interesting to note that in this preparation sodium hydroxide gives better results than potassium hydroxide.

The preparation of the corresponding chloro-arsine is readily effected by treating the iodo-compound with the calculated amount of sodium hydroxide, washing the oily oxide so obtained with water, and subsequently shaking repeatedly with small quantities of concentrated hydrochloric acid. The oil, after being dried over calcium chloride, distils at 113·5°/14 mm. (Found: Cl=17·6. C_7H_8ClAs requires Cl=17·5 per cent.).

Phenylmethylchloroarsine is a pale yellow liquid resembling phenyldichloroarsine in appearance and physiological properties.

The so-called Bart reaction (D.R.-P. 250264) for the preparation of arsinic acids is unsatisfactory in the case of phenylmethylarsinic acid, and therefore of its reduction products, although a small quantity of phenylmethyliodoarsine was prepared in this manner, benzenediazonium chloride being combined with methylarsenious oxide in alkaline solution.

The ethylation of phenylarsenious oxide proceeds very much more slowly than the methylation, and is only partial under conditions that allow of quantitative methylation.

Phenyldimethylarsine.

This arsine was obtained in 75 per cent. yield by Winmill (T., 1912, **101**, 722) by the action of magnesium methyl iodide on phenyldichloroarsine in the presence of light petroleum. The following method gave even more satisfactory results.

A Grignard reagent, made by the interaction of 19 grams of bromobenzene, 2·9 grams of magnesium, and 50 c.c. of ether, was gradually treated with a solution of 23·2 grams of dimethyliodoarsine in 50 c.c. of ether. A vigorous reaction accompanied each addition of iodo-compound, and, after allowing the mixture to remain at the ordinary temperature for two hours, ice and dilute hydrochloric acid were added, the ethereal layer separated, and dried over anhydrous sodium sulphate. The ether was evaporated and the residue distilled under diminished pressure, when 16 grams of phenyldimethylarsine were obtained as a colourless oil boiling at 85°/14 mm., and possessing the properties ascribed to the arsine by Michaelis and Link (*Annalen*, 1881, **207**, 205). The methiodide melted at 250° (Michaelis and Link, *loc. cit.*, give 244°).

The *ethiodide* is obtained at water-bath temperatures, and crystallises from alcohol in colourless needles melting at 142°; mixtures with the methiodide of phenylmethylethylarsine melted at the same temperature, indicating the identity of the two substances.

The *benziodide* is readily formed, and crystallises from a mixture of acetone and ether in colourless needles melting at 115—116° (Found: I = 31·5. $C_{15}H_{18}IAs$ requires I = 31·8 per cent.).

Phenyldimethylarsine combines energetically with equimolecular quantities of certain halogenated arsines.

Compound, $PhMe_2As,MeAsI_2$.—This compound is formed from the arsine and methyldi-iodoarsine when the two substances are

mixed in equimolecular quantities. Heat is generated, and, after a few moments, the whole becomes solid. The product crystallises from a mixture of acetone and ether in lemon-yellow needles melting at 93—94° (Found: I = 48·3. M.W. [by cryoscopic method in benzene] = 259, 264. $C_9H_{14}I_2As_2$ requires I = 48·3 per cent. M.W. = 526).

The compound is therefore completely dissociated into phenyldimethylarsine and methyldi-iodoarsine in benzene solution at concentrations up to 5 per cent.

Action of Methyl Iodide on the Compound, $PhMe_2As,MeAsI_2$.

A solution of a small quantity of the compound in benzene, mixed with an excess of methyl iodide, deposited, after some hours, slender, colourless needles, which melted at 243° without purification, a mixture with pure phenyltrimethylarsonium iodide melting at 248°. The additive compound is quantitatively converted by methyl iodide into the methiodide of the arsine originally used.

Compound, $PhMe_2As,EtAsI_2$.—Phenyldimethylarsine combines readily with ethyldi-iodoarsine to give a yellow solid, which, when crystallised from alcohol, melts at 44° (Found: I = 47·2. M.W. [by cryoscopic method in benzene] = 264, 266. $C_{10}H_{16}I_2As_2$ requires I = 47·0 per cent. M.W. = 540).

Compound, $PhMe_2As,PhAsI_2$.—This compound, prepared by mixing the arsine and iodo-arsine in calculated quantities, crystallises from alcohol or acetone in orange-coloured prisms melting at 69° (Found: I = 43·3. M.W. [by cryoscopic method in benzene] = 286, 287. $C_{14}H_{16}I_2As_2$ requires I = 43·2 per cent. M.W. = 588).

This compound is of a deeper shade than those of the corresponding compounds from alkyldi-iodoarsines.

Compound, $PhMe_2As,PhAsCl_2$.—Phenyldimethylarsine combines readily with phenyldichloroarsine to give a colourless solid crystallising from alcohol in colourless needles melting at 36° (Found: Cl = 17·7. M.W. [by cryoscopic method in benzene] = 215, 212. $C_{14}H_{16}Cl_2As_2$ requires Cl = 17·5 per cent. M.W. = 405).

Phenyldiethylarsine.

Michaelis and La Coste (*Annalen*, 1880, **201**, 212) first obtained this arsine from zinc diethyl and phenyldichloroarsine in ethereal solution, Winmill (*loc. cit.*) subsequently showing that the reaction proceeded more satisfactorily in the presence of light petroleum. We have now by the following method eliminated the difficulty attached to these methods of preparation.

A Grignard reagent, prepared from 26·2 grams of ethyl bromide,

5·8 grams of magnesium, and 40 c.c. of ether, was gradually treated with a solution of 22·3 grams of phenyldichloroarsine in 100 c.c. of benzene, the mixture finally heated to boiling for two hours, and the ether allowed to distil off slowly. The resulting mixture was decomposed with ice and dilute sulphuric acid, the benzene layer separated, dried, and evaporated, and the residue distilled under diminished pressure, when 12 grams of phenyldiethylarsine were obtained as a colourless oil boiling at 111—115°/14 mm., a further 3 grams of slightly less pure arsine distilling at 115—120°/14 mm. The arsine possessed the properties ascribed to it in the literature.

The methiodide was described by Michaelis (*Annalen*, 1902, **320**, 296) as melting at 122°. We have been unable to confirm his statements, our results being as follows.

When phenyldiethylarsine and methyl iodide are mixed, heat is evolved and a dark oil separates, which only becomes crystalline after a considerable time or after scratching vigorously. This substance, after thorough purification by repeated crystallisation from alcohol, in the presence or absence of ether, was obtained as a colourless, crystalline solid melting at 75—77° (Found: I=36·1. $C_{11}H_{18}IAs$ requires I=36·1 per cent.).

The ethiodide and the methylene iodide additive compound were found to possess the properties ascribed to them by Michaelis (*loc. cit.*).

Compound, $PhEt_2As,MeAsI_2$.—This was formed readily, and crystallised from alcohol or acetone in bright yellow needles melting at 78—79° (Found: I=45·4. M.W. [by cryoscopic method in benzene]=271, 273. $C_{11}H_{18}I_2As_2$ requires I=45·8. M.W.=544).

Phenylmethylethylarsine.

Phenylmethyliodoarsine or the corresponding chloro-compound reacts vigorously with magnesium ethyl bromide to give the desired mixed arsine.

Phenylmethyliodoarsine (19 grams) dissolved in 50 c.c. of benzene was gradually added to a Grignard reagent, prepared from 7·8 grams of ethyl bromide, 1·7 grams of magnesium, and 20 c.c. of ether. When the whole of the iodo-compound had been added, the mixture was heated to boiling for two hours, decomposed, and worked up in the usual manner, when 8 grams of phenylmethylethylarsine were obtained as a colourless oil boiling at 97°/12—13 mm. (Found [by Ewins' method]: As=37·8. $C_9H_{13}As$ requires As=38·3 per cent.).

The arsine, as might be expected, possesses physical and chemical

properties intermediate between those of the dimethyl- and diethyl-arsine.

The *methiodide* is readily formed, and crystallises from alcohol in colourless needles melting at 142° (Found: I = 37·5. $C_{10}H_{16}IAs$ requires I = 37·6 per cent.).

Compound, $PhMeEtAs,MeAsI_2$.—This compound crystallises from alcohol in yellow needles melting at 84° (Found: I = 46·8. $C_{10}H_{16}I_2As_2$ requires I = 47·0 per cent.).

Compound, $PhMeEtAs,PhAsI_2$.—This substance separates from alcohol in orange-yellow prisms melting at 55° (Found: I = 42·3. M.W. [by cryoscopic method in benzene] = 315, 322, 327. $C_{15}H_{18}I_2As_2$ requires I = 42·2 per cent. M.W. = 602).

Diphenylmethylarsine.

The preparation of this arsine by the action of zinc dimethyl on diphenylchloroarsine (Michaelis and Link, *loc. cit.*) is less satisfactory than the following.

A Grignard reagent, prepared from 34·6 grams of bromobenzene, 5·4 grams of magnesium, and 80 c.c. of ether, was gradually treated with 34 grams of methyldi-iodoarsine after removal of unchanged magnesium by decantation. The product was worked up in the usual manner, and gave 17·5 grams of diphenylmethylarsine boiling at 163—170°/15 mm., and possessing the properties described in the literature.

This arsine possesses only to a slight degree the property of forming additive compounds, and, so far, no compounds have been obtained with alkyl- or phenyl-di-iodoarsines.

The *benziodide* melts at 193° (Found: I = 27·5. $C_{20}H_{20}IAs$ requires I = 27·5 per cent.).

α-Naphthyldimethylarsine.

Dimethyliodoarsine (46·4 grams) was gradually added to a Grignard reagent, prepared from 50 grams of α-bromonaphthalene, 5·34 grams of magnesium, and 200 c.c. of ether (if small quantities of ether are used, the magnesium α-naphthyl bromide separates out as a crystalline solid), the reaction allowed to become complete by heating to boiling for an hour, and the cooled product decomposed and worked up in the usual manner. In this way, 37 grams (instead of the theoretical quantity of 46 grams) of α-naphthyldimethylarsine were obtained boiling at 163—165°/13 mm.

The *methiodide* is formed very readily, and crystallises from alcohol in colourless needles melting at 230° (Found: I = 33·7. $C_{13}H_{16}IAs$ requires I = 34·0 per cent.).

The *ethiodide* is formed at 90—100°, and crystallises from alcohol in colourless leaflets melting at 218° (Found: I=32·5. $C_{14}H_{18}IAs$ requires I=32·7 per cent.).

Compound, $C_{10}H_7·Me_2As,MeAsI_2$.—This compound is readily formed, and crystallises from alcohol in yellow needles melting at 76—77° (Found: I=44·0. $C_{13}H_{16}I_2As_2$ requires I=44·1 per cent.).

Triphenylarsine.

Although triphenylarsine is readily prepared by the action of sodium on a mixture of chlorobenzene and arsenic chloride, the following method has been found to be the most convenient for the preparation of small quantities. More than 90 per cent. of the theoretical conversion can be effected, and the arsine requires very little purification.

Powdered arsenic iodide (22 grams) was gradually added, with shaking, to a Grignard reagent, prepared from 26 grams of bromobenzene, 4 grams of magnesium, and 50 c.c. of ether. The vigorous reaction having abated, the mixture was heated to the boiling point for half an hour, and then decomposed, etc., the more volatile products being removed by heating finally to 200° under 12 mm. pressure. The residue, practically pure triphenylarsine, when once crystallised from alcohol, melted correctly at 58°.

No additive compounds could be obtained between the arsine and any of the di-iodoarsines, a fact which falls in line with the difficulty of preparing the methiodide.

Tri-o-tolylarsine.

Arsenic iodide (22·8 grams) was added gradually to a Grignard reagent, prepared from 26 grams of *o*-bromotoluene, 3·7 grams of magnesium, and 80 c.c. of ether, the reaction completed by heating for a short time, and the product worked up as in the case of triphenylarsine. Ten grams of *tri-o-tolylarsine* were obtained, and were crystallised from alcohol, when colourless needles were formed melting at 98° (Found: As=20·9. $C_{21}H_{21}As$ requires As=21·5 per cent.).

The *methiodide* crystallises from water in colourless needles melting at 166°. Owing to the small quantity of material available for analysis, the determination of iodine was unsatisfactory (Found: I=24·2. $C_{22}H_{24}IAs$ requires I=25·9 per cent.).

Di-o-tolylmethylarsine.

A Grignard reagent was prepared from 22 grams of *o*-bromotoluene, 3·2 grams of magnesium, and 50 c.c. of ether. A solution of 18 grams of methyldi-iodoarsine in 100 c.c. of benzene was gradually added, the reaction completed by heating under reflux, and the product decomposed with ice and dilute sulphuric acid. The separated ether–benzene layer was washed with aqueous sodium hydroxide to remove unchanged methyldi-iodoarsine, dried over calcium chloride, evaporated, and the residue distilled under diminished pressure. In this way, 8 grams of a very pale yellow oil were obtained boiling at 178—182°/12 mm., and setting, on cooling, to a solid melting at 42° (Found: As = 27·3. $C_{15}H_{17}As$ requires As = 27·6 per cent.).

The *methiodide* is formed readily, and crystallises from water in colourless needles melting at 195° (Found: I = 31·2. $C_{16}H_{20}IAs$ requires I = 30·7 per cent.).

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SYDNEY. [*Received, September 27th*, 1920.]

CL.—*Derivatives of Phenyldihydroresorcin.*

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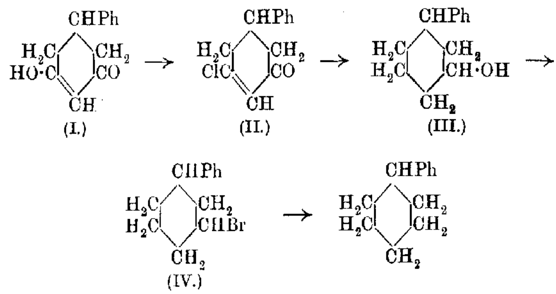
THE following is a brief account of some experiments commenced by one of us (A. J. B.) in 1914 at the suggestion of Professor A. W. Crossley: the work was interrupted, and could not be resumed until October, 1919, and although we (P. H. C. and M. E. P.) cannot now complete the original plan, it is thought advisable briefly to place on record such results as have been obtained.

The original object of the work was twofold; first, more fully to examine certain derivatives of phenyldihydroresorcin, because some of them, notably phenyl*cyclo*hexanol, had been encountered in the course of other experimental work then in progress (compare Crossley and Renouf, T., 1915, **107**, 608), and, secondly, to investigate the influence and behaviour of aromatic groups, such as phenyl, in hydroaromatic hydrocarbons. Phenyldihydroresorcin was therefore converted into phenyl*cyclo*hexane by a series of reactions which had been successfully employed in previous cases

(Crossley and Renouf, T., 1905, **87**, 1488). The dihydroresorcin (I), when treated with phosphorus trichloride, readily yields *chlorophenyl*cyclo*hexenone* (II), which, on reduction with sodium in moist ethereal solution, gives phenyl*cyclo*hexanol (III).



Hydrogen bromide converts the alcohol into *bromophenyl*cyclo*hexane* (IV), in which substance the bromine is readily displaced by hydrogen under the influence of zinc dust in aqueous-alcoholic solution, giving rise to phenyl*cyclo*hexane. The hydrocarbon is easily obtained in about 74 per cent. of the theoretical amount, and has all the properties previously ascribed to it by other workers.

Certain other derivatives of phenyldihydroresorcin were of necessity isolated in the course of the work, and they are described in the experimental part of this communication.

EXPERIMENTAL.

Phenyldihydroresorcin was prepared from ethyl malonate and styryl methyl ketone (benzylideneacetone), using the conditions described by Crossley and Renouf (T., 1915, **107**, 608). The latter was obtained from benzaldehyde and acetone, as described by Claisen and Ponder (*Annalen*, 1884, **223**, 139), but it was found that two vacuum distillations did not remove entirely the unchanged benzaldehyde, and the following procedure was therefore adopted to purify the ketone. The crude product was distilled once in a vacuum, and the distillate, which crystallised on cooling, was broken up, spread on a porous plate, and exposed to the air for two days. This caused oxidation of the benzaldehyde to benzoic acid, which was removed by washing with dilute sodium hydroxide solution. After further washing with water, the ketone was dried and crystallised from light petroleum (b. p. 60—80°).

Action of Bromine on Phenyldihydroresorcin.—Five grams of phenyldihydroresorcin (1 mol.) were suspended in 50 c.c. of dry chloroform, and a solution of 4·3 grams (2 atoms) of bromine in dry chloroform was gradually added with constant shaking, when the resorcin gradually dissolved. On further addition of bromine, much hydrogen bromide was evolved, and a bulky, white solid separated, which was collected, washed with chloroform, dried on a porous plate, and crystallised from aqueous alcohol (Found: Br = 29·95. $C_{12}H_{11}O_2Br$ requires Br = 29·96 per cent.).

4-Bromophenyldihydroresorcin, $CHPh{<}{}^{CH_2 \cdot CO}_{CH_2 \cdot CO}{>}CHBr$, crystallises from aqueous alcohol in compact clusters of short, glistening needles melting at 177° with rapid evolution of gas. (If heated sufficiently rapidly, the melting point may be found as high as 189°.) It is soluble in alcohol, acetone, or ethyl acetate, sparingly so in chloroform or benzene on boiling, but insoluble in ether or light petroleum.

Oxidation of Phenyldihydroresorcin.—Five grams of the resorcin were suspended in 125 c.c. of water and treated with a 4 per cent. solution of potassium permanganate until the latter was no longer decolorised, the whole being continuously mechanically shaken. About five hours were required for the completion of the oxidation. The product, worked up in the usual way, gave 3·8 grams of a solid, from which were isolated, by repeated recrystallisation from dilute hydrochloric acid, two acids, *A* and *B*.

The acid *A* melted at 139°, nor was this melting point lowered on admixture with a specimen of pure β-phenylglutaric acid prepared for purposes of comparison (see p. 1387).

The acid *B* melted at 166·5—167°, and its melting point was not lowered when mixed with phenylsuccinic acid (see p. 1386 for the proof of the identity of this acid).

Owing to the great similarity in solubility of β-phenylglutaric acid and phenylsuccinic acid, it was not found possible to separate the whole of *A* and *B*, but there was no evidence of the presence of another compound in the remaining mixture.

Action of Phosphorus Trichloride on Phenyldihydroresorcin.—Sixty grams (3 mols.) of phenyldihydroresorcin were heated with 22 grams (1·5 mols.) of phosphorus trichloride and 240 grams of dry chloroform on a water-bath for three hours. After distilling off the chloroform, the residue was poured into cold water and extracted four times with ether, the ethereal solution thoroughly washed with sodium hydroxide solution (4 per cent.), then with water, dried over calcium chloride, and the ether evaporated. The oily residue, which readily solidified on cooling, was crystallised

twice from light petroleum (b. p. 60—80°) (Found: Cl=17·00. $C_{12}H_{11}OCl$ requires Cl=17·19 per cent.).

5-*Chloro*-1-*phenyl*-Δ^4-cyclo*hexen*-3-*one*, $CHPh<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CCl\end{matrix}>CH$, the yield of which is about 65 per cent. of the theoretical, crystallises in colourless, transparent plates melting at 63·5—64°. It possesses a rather pungent odour, is somewhat sternutatory, and has an irritating effect on the skin. It is soluble in alcohol, ether, chloroform, acetone, benzene, or ethyl acetate, and in light petroleum on boiling. When boiled with absolute alcohol, and the solution allowed to remain in a moist atmosphere for several days, the ketone reverts to phenyldihydroresorcin. There is evidence that the ethyl ether of phenyldihydroresorcin (Vorländer and Erig, *Annalen*, 1897, **294**, 304) is an intermediate product, but the change has not been fully investigated.

The *oxime* crystallises from alcohol in almost colourless, short needles, melting and decomposing at 157° (Found: N=6·5. $C_{12}H_{12}ONCl$ requires N=6·32 per cent.).

The *semicarbazone*, prepared in the usual manner, crystallises from alcohol in rosettes of small, colourless needles. When heated in a capillary tube, it softens at 150·5°, melts at 153·5°, and decomposes at 191°. It is insoluble in the usual organic solvents, with the exception of ether, benzene, and light petroleum, in which it is only very sparingly soluble, even on boiling (Found: N=15·91. $C_{13}H_{14}ON_3Cl$ requires N=15·94 per cent.).

*Oxidation of Chlorophenyl*cyclo*hexenone*.—Twenty grams of the chloro-ketone were suspended in 500 c.c. of water and treated with a 4 per cent. solution of potassium permanganate until the latter was no longer decolorised, the whole being continuously shaken mechanically. Oxidation took place slowly, requiring twenty hours for completion. The product, worked up in the usual way, gave 13·5 grams of solid, from which were isolated, by repeated recrystallisation from dilute hydrochloric acid solution, *A*, an acid melting at 167°; *B*, an acid melting at 138·5—139·5°; and *C*, a small quantity of an acid melting at 121—121·5°, which was obtained by extraction of the above mixture with cold benzene and recrystallisation of the residue obtained on evaporation of the solvent.

The acid (*A*) yielded an anhydride melting at 53—54° and an anilic acid melting at 169—170° when treated according to the directions given by Hann and Lapworth (T., 1904, **85**, 1366) for the preparation of these derivatives of phenylsuccinic acid. The fact that these data coincide with those given by Hann and Lapworth proves the acid (*A*) to be phenylsuccinic acid.

The melting point of the acid *B* was not lowered on admixture with pure β-phenylglutaric acid (m. p. 138—140°) prepared for the purposes of comparison (*Ber.*, 1899, **32**, 1879). On treating its silver salt with methyl iodide in dry ethereal solution, an ester resulted melting at 83·5—84·5°, nor was this melting point lowered on admixture with a specimen of the pure dimethyl ester of β-phenylglutaric acid (m. p. 84—85°) prepared for the purposes of comparison (*Ber.*, 1898, **31**, 1828).

Only a very small quantity of the acid *C* was obtained after recrystallisation from water. On admixture with pure benzoic acid, the melting point was not lowered appreciably, and, although the amount of the acid was too small to admit of further purification or preparation of derivatives, its odour and behaviour towards various solvents support the supposition that it is benzoic acid.

*Reduction of Chlorophenyl*cyclo*hexenone.*—Quantities of 20 grams of the chloro-ketone were treated with twice the calculated quantity of sodium in moist ethereal solution, as described by Crossley and Renouf (T., 1905, **87**, 1494). When all the sodium had dissolved, the ethereal solution was separated, washed with water until no longer alkaline, dried over anhydrous potassium carbonate, and the ether evaporated. The residue was submitted to steam distillation until a test portion of the distillate gave no turbidity on adding potassium carbonate. The distillate contained a solid in suspension, crystallising in colourless needles, which were collected and crystallised from light petroleum (b. p. 80—100°) (Found: C=81·60; H=9·36. $C_{12}H_{16}O$ requires C=81·76; H=9·16 per cent.).

1-Phenyl*cyclo*hexan-3-ol, $CHPh{<}{\begin{matrix}CH_2\cdot CH(OH)\\CH_2\text{———}CH_2\end{matrix}}{>}CH_2$, was prepared, although not fully described, by Crossley and Renouf (T., 1915, **107**, 608) for comparison with a by-product obtained in the reduction of phenyldihydroresorcin. It is obtained in 50—53 per cent. of the theoretical amount, and crystallises in fine, colourless needles melting at 79·5—80·5°, and possessing a pleasant odour somewhat resembling that of geranium. It is soluble in the usual organic solvents, but only sparingly so in cold light petroleum. When dissolved in absolute alcohol and the solution gradually treated with concentrated sulphuric acid, it gives a greenish-yellow colour, slowly changing to brown with a green fluorescence.

The *acetyl* derivative, prepared in the usual manner, crystallises from a small quantity of alcohol in stout, transparent, oblong plates melting at 43—44°, and is readily soluble in all the usual organic solvents. It can be distilled in air without decomposition

and boils at 300° (Found: C=77·05; H=8·69. $C_{14}H_{18}O_2$ requires *C=77·01; H=8·32 per cent.*).

The *benzoyl* derivative is readily obtained in quantitative yield. It crystallises from ethyl or methyl alcohol in rosettes of colourless prisms melting at 68°, and is readily soluble in all the usual organic solvents on boiling (Found: C=81·28; H=7·36. $C_{19}H_{20}O_2$ requires C=81·39; H=7·19 per cent.).

The o-*nitrobenzoyl* derivative was prepared by allowing molecular proportions of *o*-nitrobenzoyl chloride and the alcohol to react in pyridine solution. It crystallises from dilute solution in ethyl or methyl alcohol in rosettes of minute needles melting at 70° (Found: N=4·49. $C_{19}H_{19}O_4N$ requires N=4·31 per cent.).

*Action of Hydrogen Bromide on Phenyl*cyclo*hexan-3-ol.*—Quantities of 5 grams of the alcohol were sealed up in small soda-water bottles with 25 c.c. of fuming hydrobromic acid, saturated at 0°, and heated in a water-bath for one hour. The resulting liquid, which was in two layers, was poured into excess of cold water, and the lower, oily portion dissolved in ether. The ethereal solution was washed with water, then with dilute sodium carbonate solution, finally again with water, dried, and the ether removed, the residue being distilled under diminished pressure (Found: Br=33·49. $C_{12}H_{15}Br$ requires Br=33·42 per cent.).

3-*Bromo*-1-*phenyl*cyclo*hexane*, the yield of which is almost quantitative, is a clear, colourless liquid boiling at 186—187°/40 mm., with a pleasant odour resembling that of geraniol, yet somewhat reminiscent of the odour of oranges.

*Action of Zinc Dust on 3-Bromo-1-phenyl*cyclo*hexane.*—Twenty-four grams of bromophenyl*cyclo*hexane were mixed with 75 c.c. of 90 per cent. alcohol and sufficient absolute alcohol to form a clear solution, to which were added 38·5 grams of zinc dust mixed with an equal volume of sand, and the whole was heated on the water-bath for ten hours. The resulting liquid was poured into a large excess of water, the mixture extracted with ether, the ethereal solution washed with water, dried, and the ether evaporated, using a fractionating column. The resulting oil, which was nearly colourless, was heated over metallic sodium for two hours and then distilled, when 13 grams passed over at 232—233°, and, after one further distillation from sodium, 11·9 grams (yield, 74 per cent. of the theoretical) were obtained boiling constantly at 233—234°/755 mm. It readily solidified when cooled to just below 0°, and melted at 6·5°. These properties agree closely with previous descriptions of the properties of phenyl*cyclo*hexane (Willstätter and Lessing, *Ber.*, 1901, **34**, 506; Eijkman,

Chem. Weekblad, 1903, **1**, 7; Meerwein and Kremers, *Annalen*, 1919, **419**, 121).

In order further to establish its identity with phenyl*cyclo*hexane, 6 grams of the substance were treated with fuming nitric acid (*D* 1·50) until the addition of acid caused no further visible change (about 10 c.c. of acid were used). The mixture was poured into water, and the heavy, oily layer dissolved in ether and worked up in the usual manner. On evaporation of the ether, 7·9 grams of a yellow oil were obtained, which, on cooling, gave a crystalline deposit weighing 3·8 grams after drying on a porous plate. It crystallised from aqueous alcohol in large, colourless, lustrous leaflets melting at 57·5—58° (Kursanov, *Annalen*, 1901, **318**, 309, gives the melting point of *p*-nitrophenyl*cyclo*hexane as 57·5—58·5°).

*Preparation of Phenyl*cyclo*hexan-3-one*, $CHPh{<}{\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}}{>}CH_2$. —Fourteen grams of phenyl*cyclo*hexan-3-ol were added to 126 grams of Beckmann's chromic acid mixture [60 grams (1 mol.) of potassium dichromate and 50 grams (2·5 mols.) of sulphuric acid in 300 c.c. of water], the whole being well shaken. The temperature rose to 45°, when a reaction set in, which was soon complete. The mixture was then kept at 50—55° for thirty minutes, with constant shaking, extracted with ether, the ethereal solution worked up in the usual way, and dried. After evaporating the ether, the residual, colourless oil was distilled under diminished pressure, when 12·7 grams passed over at 169—169·5°/18 mm. (Found: C = 82·52; H = 8·42. $C_{12}H_{14}O$ requires C = 82·72; H = 8·10 per cent.).

1-*Phenyl*cyclo*hexan-3-one*, the yield of which is practically quantitative, is a colourless liquid boiling at 169—169·5°/18 mm. and 287—288°/736 mm., which does not solidify when cooled to −10°. With alcoholic sulphuric acid it gives a reddish-yellow solution with a green fluorescence.

The *semicarbazone*, prepared in the usual manner, crystallises from alcohol in radiating clusters of glistening prisms melting at 167°. It is soluble in methyl or ethyl alcohol, chloroform, or ethyl acetate, and in acetone, benzene, or light petroleum on boiling, but only very sparingly so in ether (Found: N = 18·22. $C_{13}H_{17}ON_3$ requires N = 18·18 per cent.).

The *oxime* crystallises from alcohol in colourless, ill-defined plates, which melt at 128—129°, but begin to shrink at about 120°. It is insoluble in light petroleum and only sparingly soluble in ether, but dissolves readily in the other usual organic

solvents, especially on warming (Found: N = 7·34. $C_{12}H_{15}ON$ requires N = 7·41 per cent.).

The authors desire to express their sincere thanks to Professor Crossley for originally suggesting the work and for the help given by him during its progress.

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CLI.—*The Electrical Conductivity of Potassium, Sodium, and Barium Chlorides in Mixtures of Pyridine and Water.*

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IN previous papers (T., 1918, **113**, 449, 627) it has been shown that in solutions of strong electrolytes, the increase in molecular conductivity with dilution is given by the following equations:

$$\frac{N.E^2\sqrt[3]{2N}}{D\sqrt[3]{V}} = 2RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for univalent binary electrolytes, and

$$\frac{6N.E^2\sqrt[3]{2N}}{D\sqrt{3}\sqrt[3]{V}} = 3RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad (2)$$

for uni-bivalent electrolytes, where N is Avogadro's number, E the absolute charge on an ion, V the molecular dilution, and D the dielectric constant of the solvent. Equations (1) and (2) contain the term μ_∞, the molecular conductivity at infinite dilution, which cannot be determined experimentally. They can, however, be easily put in the following forms, which contain no unknown magnitudes whatsoever:

$$\frac{N.E^2\sqrt[3]{2N}}{D.2RT}\left\{\frac{1}{\sqrt[3]{V_1}} - \frac{1}{\sqrt[3]{V_2}}\right\} = \log_e\frac{\mu_{v_2}}{\mu_{v_1}} \quad - \quad . \quad . \quad . \quad (3)$$

and

$$\frac{6N.E^2.\sqrt[3]{2N}}{D.\sqrt{3}.3RT}\left\{\frac{1}{\sqrt[3]{V_1}} - \frac{1}{\sqrt[3]{V_2}}\right\} = \log_e\frac{\mu_{v_2}}{\mu_{v_1}} \quad - \quad . \quad . \quad . \quad (4)$$

The present investigation was carried out with the object of testing the validity of the above relation between the dielectric constant of the solvent and variation of molecular conductivity with dilution.

It has already been shown that the extensive experimental data of Walden on the molecular conductivity of tetraethylammonium iodide in various solvents can be accounted for (with the exception of the aldehydes) on the assumption that tetraethylammonium iodide at first undergoes polymerisation, and then the double molecule dissociates as a uni-bivalent electrolyte. The experimental difficulties in determining molecular conductivity in pure non-aqueous solvents are very great. The data of different observers do not very often agree at all, and it was therefore concluded that the agreement between the observed and calculated value of molecular conductivity was within the limits of experimental error. In the present investigation, only the chlorides of potassium, sodium, and barium were used, which, unlike the iodide, have very little tendency to complex-formation. Binary mixtures of pyridine and water were selected, as they are completely miscible in one another, and offer a very wide range of dielectric constants varying from 12 to 80.

Preparation of Materials.

Chemically pure pyridine was distilled several times over solid potassium hydroxide, and the fraction distilling at 115—116° was collected. This fraction was then allowed to remain overnight over pieces of metallic sodium, as recommended by Hopkins (this vol., p. 280). Gas bubbles were evolved, showing that moisture was present. The dry substance was distilled directly into a dry flask protected from moisture by a calcium chloride tube. The specific conductivity at 18° was $0{\cdot}2 \times 10^{-6}$ mho, and the boiling point 115·6°.

Water was purified by distillation from acid and alkaline permanganates, a block-tin condenser being used. It was finally distilled from a quartz distillation apparatus, and stored in quartz flasks. The specific conductivity of the water was $1{\cdot}2 \times 10^{-6}$ mho at 18°. The mixtures of pure pyridine and water were also stored in quartz flasks.

The salts were crystallised twice from pure samples and dried by heating in a platinum crucible.

For experiments at 0°, a bath containing finely powdered ice was used, jacketed by a second vessel containing ice. The temperature varied from 0° to 0·05°. For experiments at 18°, a thermostat was used, the extreme variation of temperature being 0·02°. For

dilutions below 1000 litres, a closed conductivity cell made of Jena resistance glass was used, and for higher dilutions, a closed quartz cell, made by the British Silica Syndicate.

The bridge wire was carefully calibrated, and the resistances were National Physical Laboratory standards of 1, 10, 100, and 1000 ohms.

Dielectric Constants of Mixtures of Pyridine and Water.

The Nernst method was employed as modified by Turner (*Zeitsch. physikal. Chem.*, 1900, **35**, 385). A Wehnelt interrupter was used in the primary circuit of the secondary coil; it consisted of two thin platinum wires dipped in dilute sulphuric acid. The anode could be raised up and down by means of a rack and pinion arrangement, and a sharp, fine tone obtained at 16 volts by careful adjustment. The dielectric constant of pure pyridine at 0°, with chemically pure benzene as the liquid for comparison, was found to be 12·5 from the equation

$$D=(D_0-1)\frac{S-s}{s_0-s}+1,$$

where D_0 is the dielectric constant of the known substance, s the number of scale divisions the condenser plate has to be moved when the vessel is empty, s_0 the number for the substance of known dielectric constant, and S for the unknown substance. For binary mixtures of water and pyridine, pure pyridine was used as the comparison liquid, and the dielectric vessel consisted of a platinum crucible, and a platinum disk attached to the end of a platinum rod passing through a hole in the ebonite cover of the crucible.

Although pure pyridine and pure water have themselves very little specific conductivity, the conductivity of the binary mixture increases with increasing proportion of water, and for a mixture containing 90 per cent. of water, it is as high as 10×10^{-6} mho at 18°. The data for the dielectric constants of the mixtures containing a large proportion of water are therefore not very accurate, as it is very difficult to get a sharp sound minimum in the telephone.

TABLE I.

Percentage by weight of pyridine in water.	Dielectric constant at 0°.	Dielectric constant at 18°.
96·0	13·0	12·5
92·5	15·3	16·0
80·0	22·9	21·0
67·0	27·7	25·1
60·0	40·0	37·0
40·0	56·4	52·2
20·0	68·3	64·1

Molecular Conductivity of Salts in Mixtures of Pyridine and Water.

Mixtures containing 80 or 60 per cent. by weight of pyridine do not dissolve the chlorides of barium, potassium, and sodium easily. A definite amount of salt was therefore first dissolved in a given quantity of pure water, and pyridine then added. Barium chloride is not very readily soluble in these mixed solvents. Even in the case of $N/40$-solutions, crystals generally separate on keeping overnight. The state of supersaturation can, however, be easily maintained for the few hours necessary for taking a complete set of readings at various dilutions.

The molecular conductivity of the solutions is rather small, and hence the correction for the conductivity of the solvent becomes quite appreciable when the dilution is 80. The accuracy of the data for higher dilution depends on this solvent correction, and it was therefore necessary to determine the specific conductivity of the solvents every few hours. In tables II, III, IV, V, VI, and VII are given the observed values of equivalent conductivities at 0° and 18°. They are compared with those calculated from the observed value of λ_{160} from equation (3) in the case of uni-

TABLE II.

$t=0°$.

Solvent containing 40 per cent. by weight of pyridine.

Salt.	$V=$	10.	40.	80.	640.	2560.
NaCl	λ obs.	22·1	24·6	25·5	27·6	28·6
	λ calc. from λ_{160} obs. = 26·3	22·5	24·8	25·6	27·4	28·1
KCl	λ obs.	25·6	28·3	29·3	31·4	32·2
	λ calc. from λ_{160} obs. = 30·0	25·9	28·2	29·2	31·1	31·8
$BaCl_2$	λ obs.	20·0	23·6	—	27·7	29·0
	λ calc. from λ_{160} obs. = 26·1	19·6	23·4	—	28·0	29·3

TABLE III.

$t=0°$.

Solvent containing 60 per cent. by weight of pyridine.

Salt.	$V=$	10.	20.	40.	80.	640.	2560.
NaCl	λ obs.	12·7	—	14·8	—	17·3	18·0
	λ calc. from λ_{160} obs. = 16·1	12·9	—	14·8	—	17·0	17·5
KCl	λ obs.	—	14·55	15·7	16·5	18·3	19·1
	λ calc. from λ_{160} obs. = 17·2	—	14·80	15·7	16·5	18·2	18·8
$BaCl_2$	λ obs.	10·2	—	12·9	—	16·1	17·0
	λ calc. from λ_{160} obs. = 14·8	9·9	—	12·7	—	16·3	17·3

TABLE IV.

$t = 0°$.

Solvent containing 80 per cent. by weight of pyridine.

Salt.	V =	20.	40.	80.	640.	5120.
NaCl	λ obs.	8·9	10·1	—	13·5	15·2
	λ calc. from λ_{160} obs. = 12·1	9·4	10·4	—	13·2	14·4
KCl	λ obs.	—	10·1	10·8	13·8	15·5
	λ calc. from λ_{160} obs. = 11·9	—	10·3	11·1	13·1	14·3

TABLE V.

$t = 18°$.

Solvent containing 40 per cent. by weight of pyridine.

Salt.	V =	10.	40.	80.	640.	2560
NaCl	λ obs.	40·4	44·6	46·5	50·1	51·8
	λ calc. from λ_{160} obs. = 47·9	40·9	45·1	46·7	49·8	51·1
KCl	λ obs.	46·8	51·5	53·8	57·8	59·4
	λ calc. from λ_{160} obs. = 55·6	47·4	52·3	54·1	57·8	59·2
$BaCl_2$	λ obs.	38·2	44·2	—	53·5	55·6
	λ calc. from λ_{160} obs. = 50·1	37·5	44·8	—	53·8	56·2

TABLE VI.

$t = 18°$.

Solvent containing 60 per cent. by weight of pyridine.

Salt.	V =	10.	20.	40.	80.	640.	2560.
NaCl	λ obs.	25·1	—	29·4	—	34·1	35·2
	λ calc. from λ_{160} obs. = 32·0	25·6	—	29·5	—	33·6	34·7
KCl	λ obs.	—	28·6	31·0	32·3	35·8	37·5
	λ calc. from λ_{160} obs. = 34·1	—	29·4	31·3	32·8	35·9	37·3
$BaCl_2$	λ obs.	19·6	—	24·9	—	31·4	33·2
	λ calc. from λ_{160} obs. = 28·7	19·1	—	24·5	—	31·7	33·8

TABLE VII.

$t = 18°$.

Solvent containing 80 per cent. by weight of pyridine.

Salt.	V =	20.	40.	80.	640.	5120
NaCl	λ obs.	17·2	19·5	—	26·3	29·9
	λ calc. from λ_{160} obs. = 23·4	18·1	20·1	—	25·8	27·9
KCl	λ obs.	—	19·1	21·0	25·0	28·9
	λ calc. from λ_{160} obs. = 22·7	—	19·5	21·2	25·2	27·3

univalent salts, and from equation (4) in the case of barium chloride. In the tables, V is the equivalent dilution in litres and λ the equivalent conductivity.

It will be noticed from the above tables that the agreement between the observed and calculated values of equivalent conductivities are within the limits of experimental error, except in the case of the solvent containing 80 per cent. by weight of pyridine. Here the extreme deviations between the observed and calculated values are as much as 7 per cent. Perhaps in the mixed solvent rich in pyridine there is a slight complex-formation. Hartley, Thomas, and Applebey (T., 1908, **93**, 538) have determined the molecular conductivity of lithium nitrate in mixtures of varying proportions of pyridine and water. It appears interesting to examine whether their experimental data agree with those calculated from equation (3). The observed values of molecular conductivity in table VIII are taken from their paper.

TABLE VIII.

$t = 25°$. Salt: Lithium Nitrate.

Mol. per cent. of pyridine in solvent.	$V =$	16.	32.	64.	128.	256.	512.	1024.
83·98	λ obs.	20·1	24·4	27·5	32·1	35·4	38·3	—
	λ calc from λ_8 obs. = 15·8	19·3	23·3	27·5	31·9	36·1	40·1	—
73·76	λ obs.	23·1	26·5	30·3	33·2	35·9	38·1	40·5
	λ calc. from λ_8 obs. = 19·1	22·9	26·8	30·3	33·8	37·0	39·6	41·6
46·67	λ obs.	24·9	27·4	29·5	30·7	32·2	33·2	—
	λ calc. from λ_8 obs. = 21·5	24·4	26·6	28·4	30·0	31·2	31·9	—
31·28	λ obs.	27·5	29·4	31·0	32·4	33·5	34·4	—
	λ calc. from λ_8 obs. = 25·2	27·4	29·1	30·4	31·4	32·2	32·5	—
5·71	λ obs.	60·8	63·1	64·9	66·3	67·5	68·5	69·5
	λ calc. from λ_8 obs. = 58·1	61·0	63·3	65·1	66·7	67·6	68·2	68·5

It will be at once seen that the agreement between the observed and calculated values of molecular conductivity is quite satisfactory. It is peculiar that in the solvent containing a 46·67 molecular percentage of pyridine, which is equivalent to 79 per cent. by weight of pyridine, the observed values of equivalent conductivity for lithium nitrate agree with the calculated values within the limits of experimental error. It is strange that the simpler salts, like potassium and sodium chlorides, should show greater deviations.

Viscosity of Mixtures of Pyridine and Water.

Hartley, Thomas, and Applebey (*loc. cit.*), and Dunstan and Thole (T., 1907, **91**, 1728), have determined the viscosity of mixtures of pyridine and water at 0° and 25°. No simple relation like that discovered by Walden between the molecular conductivity and viscosity of the solvent in solutions of tetraethylammonium iodide exists here. Following the lead of Bousfield, Hartley, Thomas, and Applebey conclude from the comparison of viscosity and conductivity data of lithium nitrate in mixtures of pyridine and water that there is a change in the size of the solvent atmosphere attached to the ions as the composition of the solvent changes. Although speculations in this field do not lead to tangible results, it was thought advisable to complete the investigation by determining the viscosities of the mixed solvents used in this investigation at 18°. For this purpose, a Dunstan and Thole type of viscosimeter was used. The results are given in table IX.

TABLE IX.

Percentage of pyridine in the solvent mixture.	Viscosity of the solvent mixture relative to water at 18°.
80	2·375
60	2·572
40	2·153

It will be observed that the conductivity of the salts continually increases as the percentage of pyridine in the solvent diminishes from 80 to 40. The viscosity of the mixture of pyridine and water, however, passes through a maximum, when the percentage by weight of pyridine is approximately 65.

Conclusion.

The molecular conductivity of the chlorides of potassium, sodium, and barium in mixtures of pyridine and water was studied. The dielectric constants of the solvents varied from 12 to 68; the experimental data confirm the hypothesis of complete ionisation of strong electrolytes as developed by the author.

My best thanks are due to Prof. F. G. Donnan, F.R.S., for his kind interest and help in providing the apparatus necessary for this investigation, and to my friend Mr. J. N. Mukherjee.

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CLII.—*The System Benzene-Ethyl Alcohol-Water between* $+25°$ *and* $-5°$.

By Nevil Vincent Sidgwick and William James Spurrell.

Several investigations have been made on parts of this system at various temperatures, but no complete study has yet been published of the conditions of separation of solid benzene from a mixture of the three components.

This question is of general theoretical interest, and also of some practical importance, in view of the use of mixtures of benzene and alcohol as motor fuel.

Considering, first, the two-component systems involved, the system water–benzene is soon disposed of. The mutual solubilities at any temperatures with which we are concerned are very small. At 23°, the solubility of water in benzene is 0·061 per cent.* (Groschuff, *Zeitsch. Elektrochem.*, 1911, **17**, 348); at 15°, that of benzene in water is 0·15 per cent. (Moore and Roaf, *Proc. Roy. Soc.*, 1905, [*B*], **77**, 96). If we assume that the solubilities change with temperature in the same proportion as the vapour pressures, their values near the triple point (5·4°) will be: water in benzene 0·082, benzene in water 0·092 per cent. The temperature of the triple point, solid benzene–liquid benzene–water, has been found to be 5·39° (Sidgwick, this vol., p. 1340)—one-tenth of a degree below the freezing point of benzene; that of the triple point, ice–water–benzene, is by calculation $-0·016°$, the solubility of the benzene at this temperature being 0·069 per cent.

The system water–alcohol also scarcely concerns us. The freezing-point curve of solutions of water in alcohol has been measured (for example, by Pickering, T., 1893, **63**, 1015); a 10 per cent. solution freezes at about $-4·6°$, but the solubility of benzene in such a solution is so small that we did not investigate the ice curve.

The system benzene–ethyl alcohol is of much greater importance. The freezing-point curve has been examined by several observers. Our own results (extrapolated for anhydrous alcohol) are nearest to those of Pickering (*loc. cit.*, p. 1019), with whom Viala (*Bull. Soc. chim.*, 1914, [iv], **15**, 5) and Rózsa (*Zeitsch. Elektrochem.*, 1911, **17**, 934) also agree fairly closely. McIntosh (*J. Physical Chem.*, 1896, **1**, 480), who also measured this curve, states that his

* All solubilities in this paper are expressed in grams of solute per 100 grams of solution.

alcohol may have contained water; from our results, it seems that it must have contained about 4 per cent.

The three-component system has been examined by McIntosh (*loc. cit.*), Taylor (*J. Physical Chem.*, 1896, **1**, 301, 461), Lincoln (*ibid.*, 1900, **4**, 176), Bonner (*ibid.*, 1910, **14**, 779), and Rózsa (*loc. cit.*). McIntosh investigated the freezing point of the benzene, and drew attention to the remarkable fact that the freezing point of benzene containing alcohol is raised by the addition of water; he correctly explained this as being due to the increase of the vapour pressure of benzene on addition of a component in which it is insoluble, but his numerical results are vitiated by the presence of water in his original alcohol. Taylor, Lincoln, and Bonner examined the two-liquid equilibrium between 10° and 25°, and determined the composition of the conjugate solutions (tie-lines). Rózsa investigated the system both above and below the freezing point; his results are difficult to understand, as he does not define his concentrations, but on the most probable hypothesis they are roughly in agreement with ours.

These results taken together give an incomplete account of the behaviour of the system in the neighbourhood of the freezing point of benzene. We have endeavoured to extend and complete them.

Experimental.

The method adopted was to prepare mixtures of alcohol and water of known strength; these were mixed with various known proportions of benzene, and the temperature was determined at which the liquid separated into two layers or the benzene crystallised out. The concentrations are always expressed in grams of component per 100 grams of solution.

The alcohol was obtained by distilling ordinary "absolute" alcohol with lime; the percentage of water in it was determined from the density, using the tables given in the last edition of Beilstein's "Handbuch der Organischen Chemie." From this, the requisite aqueous mixtures were prepared gravimetrically. The purest alcohol used (99·5 per cent.) was obtained from this by redistillation after treatment with anhydrous copper sulphate.

The benzene was freed from thiophen by sulphuric acid, and frozen out seven times; it was then distilled over sodium.

The apparatus consisted of an ordinary Beckmann tube with air-jacket, thermometer, and stirrer. A known weight of one of the liquids was placed in it, and successive amounts (usually 1 c.c.) of the other added through the side-tube from an accurate pipette, which had been carefully graduated by weight with the particular

liquid to be used in it. The tube was warmed or cooled by a bath of water, ice, or ice and salt.

The thermometers had been compared with an instrument standardised at the Reichsanstalt, and were checked by redeterminations of the ice-point. The readings were corrected, when necessary, for the emergent stem. At high concentrations of benzene, the method of supercooling could be used, as the amount of solid benzene separating did not seriously affect the proportions. At lower concentrations, the point was observed at which the last

TABLE I.

Alcohol, 99·5 per cent.

Benzene. Per cent.	Temp.
92·42	+2·95°
80·29	1·26
75·32	0·50
70·92	−0·14
67·05	−0·86
62·05	−1·94
57·85	−2·94
54·16	−4·16
50·95	−5·42

Alcohol, 98·0 per cent.

Benzene. Per cent.	Temp.
95·20	+3·50
93·09	3·10
91·12	2·76
86·86	2·22
81·82	1·62
77·15	1·08
69·23	0·03
65·56	−0·72
58·76	−2·16
53·30	−3·90
50·55	−4·62
48·30	−5·72

Alcohol, 95·76 per cent.

Benzene. Per cent.	Temp.
94·50	+3·48
89·60	2·84
81·15	1·86
77·51	1·48
65·70	0·12
59·35	−1·04
55·46	−1·92
52·04	−2·75
49·02	−3·62
46·34	−4·42
43·94	−5·34

Alcohol, 90·06 per cent.

Benzene. Per cent.	Temp.
89·18	+30·7 (*L*)
87·55	26·1 (*L*)
86·88	23·9 (*L*)

Alcohol, 90·06 per cent.—*contd.*

Benzene. Per cent.	Temp.
85·24	16·1° (*L*)
84·30	11·0 (*L*)
83·18	5·2 (*L*)
82·54	2·0 (*L*)
81·19	2·51
74·22	2·13
68·33	1·78
59·42	0·95
55·60	0·42
49·31	− 0·51
46·62	− 0·91
42·09	− 1·97
37·65	− 3·54
35·76	− 4·30
34·05	− 5·14

Alcohol, 86·0 per cent.

Benzene. Per cent.	Temp.
73·89	+28·3 (*L*)
72·81	22·7 (*L*)
71·63	17·6 (*L*)
70·35	12·9 (*L*)
68·93	8·5 (*L*)
67·38	4·5 (*L*)

Alcohol, 80·10 per cent.

Benzene. Per cent.	Temp.
63·52	+39·2 (*L*)
61·66	32·1 (*L*)
57·41	19·6 (*L*)
50·55	9·2 (*L*)
47·14	5·2 (*L*)
44·19	1·6 (*L*)
44·19	2·45
39·24	2·00
33·03	0·96
30·64	0·30
26·78	− 1·12
25·18	− 2·02
23·76	− 2·97
22·50	− 3·75
21·36	− 4·67

Alcohol, 74·48 per cent.

Benzene. Per cent.	Temp.
44·43	+29·5° (*L*)
38·23	20·3 (*L*)
35·12	15·2 (*L*)
31·02	7·75 (*L*)
28·90	3·00 (*L*)
27·04	− 1·25 (*L*)
27·04	+ 2·30
24·03	+ 1·20
18·64	− 2·25
17·65	− 3·10
15·96	− 4·85

Alcohol, 69·08 per cent.

Benzene. Per cent.	Temp.
27·67	+25·3 (*L*)
25·88	21·2 (*L*)
24·31	17·3 (*L*)
22·91	13·5 (*L*)
21·67	9·9 (*L*)
20·55	6·5 (*L*)
19·06	1·95 (*L*)
18·20	2·30
17·15	1·52
15·37	0·02
13·72	− 1·34
12·37	− 3·02
11·81	− 3·70

Alcohol, 57·66 per cent.

Benzene. Per cent.	Temp.
10·53	+15·4 (*L*)
10·05	12·15 (*L*)
9·25	7·1 (*L*)
8·56	2·3 (*L*)
8·27	− 0·40 (*L*)
8·27	+ 2·15
6·66	− 2·92
6·34	− 4·20

Alcohol, 39 per cent

Benzene. Per cent.	Temp.
Less than 1·0	+25·0 (*L*)

crystals remained in equilibrium with the liquid. For the two-liquid equilibria, the point was taken at which the liquid, on slow cooling, became sufficiently turbid to obscure a bright object placed behind it.

The results are given in table I (p. 1399). The temperature is in every case the mean of two or three concordant observations; these, in the solutions containing more benzene, did not differ by more than 0·1°, but in the weaker solutions differences of as much as 0·25° could not always be avoided.

Each series in the table was carried out with alcohol of the strength stated at the head; the percentage of benzene given in the first column is the number of grams in 100 grams of the resulting mixture. The points marked (*L*) are those in which the separation was into two liquids; in all other cases they are the freezing points of the benzene. One or two solutions gave points of both kinds, a higher (stable) solid and a lower (metastable) liquid point.

From the curves, the values for a series of round temperatures were interpolated, and these are collected in table II. The first column gives the temperature, the second the freezing points of mixtures of benzene and anhydrous alcohol from the results of Pickering (*loc. cit.*); the other columns are from our own experiments. The two-liquid points are distinguished by an asterisk. The total composition of any liquid is, of course, obtained thus: the percentage of benzene is that given in the table; the percentage of water or alcohol is obtained by multiplying the difference between this and 100 by the proportion of water or alcohol (from the figure at the top of the column) in the aqueous alcohol used. At the foot of each column is given the percentage of benzene and the temperature at the triple point solution I–solution II–solid benzene.

The results are plotted for temperatures from +5° to −5° in Fig. 1, the full lines representing two-liquid and the dotted lines liquid–solid equilibria.

Discussion of Results.

The equilibrium of a three-component system can be expressed only by a solid diagram; this can take the form of a triangular prism, the isothermal curves being represented on a series of triangles. Each of the curves obtained by adding varying quantities of benzene to aqueous alcohol of a definite strength (which are plotted in Fig. 1) represents a section of this solid diagram by a plane which contains the temperature axis passing through the

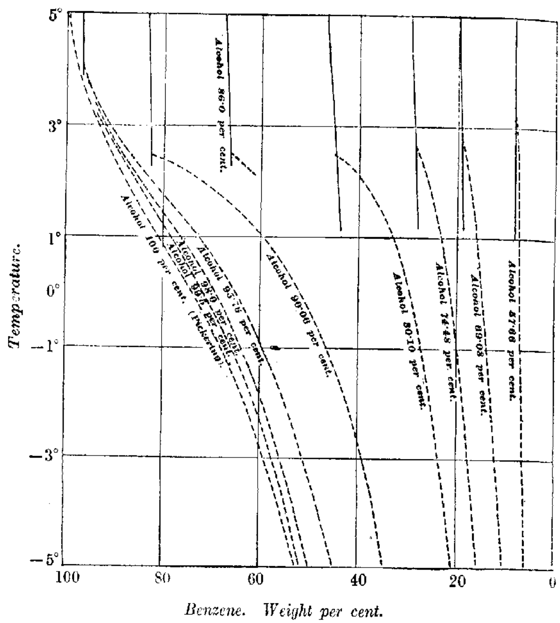
TABLE II.

The first line gives the percentage of alcohol in the mixture of alcohol and water employed, the other figures the percentage of benzene in the liquid at equilibrium.

Alcohol, per cent.:	100 Pickering	99·5	98·0	95·76	90·06	86·0	80·10	74·48	69·08	57·66	39·0
25°	—	—	—	—	87·22*	73·25*	59·41*	41·32*	27·46*	12·61*	1·0*
15	—	—	—	—	85·05*	70·95*	55·00*	35·10*	23·38*	10·47*	—
5	99·48	—	—	—	83·05*	67·65*	46·92*	29·81*	20·08*	8·95*	—
4	97·57	—	—	—	82·95*	—	46·18*	29·32*	19·75*	8·81*	—
3	93·82	92·65	92·52	91·22	82·76*	—	45·42*	28·85*	19·45*	8·68*	—
3	—	—	—	—	—	—	—	—	—	8·61	—
2	87·90	85·28	85·06	82·64	71·90	—	39·24	26·00	17·70	8·21	—
2	—	—	—	—	82·55*	—	44·50*	28·46*	19·10*	8·55*	—
1	80·89	78·36	76·58	72·78	59·80	—	33·15	23·60	16·45	7·86	—
1	—	—	—	—	82·35*	—	43·70*	27·95*	18·78*	8·44*	—
0	74·08	71·87	69·25	65·03	52·01	—	29·85	21·74	15·35	7·53	—
0	—	—	—	—	82·10*	—	43·08*	27·59*	18·48*	8·32*	—
−1	67·79	66·45	63·93	59·48	46·39	—	27·34	20·11	14·25	7·22	—
−2	62·87	61·70	59·62	55·07	42·00	—	25·40	18·93	13·27	6·93	—
−3	59·10	57·54	56·00	51·17	39·00	—	23·52	17·80	12·40	6·65	—
−4	55·56	54·49	52·71	47·82	37·48	—	22·21	16·75	11·56	6·38	—
−5	52·60	51·85	49·90	44·81	34·45	—	21·00	15·82	10·80	6·12	—
Triple Point	—	—	—	96·76 +4·10°	82·62 +2·55°	66·38 +2·52°	44·95 +2·50°	28·75 +2·64°	19·28 +2·86°	8·70 +3·20°	— —

benzene edge of the prism, and cuts the opposite side along a vertical line corresponding with the particular mixture of alcohol and water employed. The isothermals for three temperatures, namely, $+25°$, $+3°$, and $-5°$, are plotted on the triangle in Fig. 2. At 25° there is, of course, only the two-liquid equilibrium represented by the innermost curve. The dotted tie-lines, giving

FIG. 1.



Full lines: Liquid–liquid equilibria.
Dotted lines: liquid–solid ,,

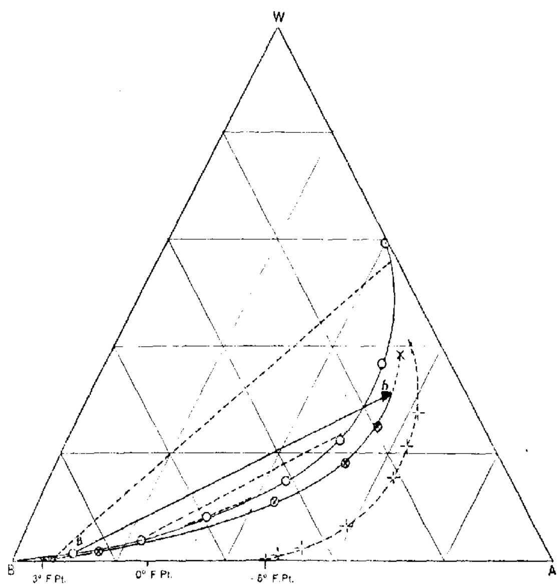
the compositions of the two liquids in equilibrium with one another, are taken from Taylor's measurements (*loc. cit.*).

At temperatures below 5·49°, solid benzene is present at *B* (pure benzene), and extends further along *BA* as the temperature falls. At $+3°$, for example, the solid is in equilibrium with a mixture of benzene and alcohol containing 6·18 per cent. of the latter. If water is added to this mixture, the freezing point of the benzene is raised, because the water, being insoluble in the benzene,

increases its vapour pressure. In order, therefore, to remain in the 3° isotherm, if water is added, alcohol must also be added; the solid–liquid curve (the dotted line) will thus incline to the right. Our results show that when it has reached the point *a*, a second

FIG. 2.

Water.



Benzene. *Alcohol.*

+25° Isotherm : ——○——
+3° Isotherm : Solid–liquid - - -×- - -
Liquid–liquid ——⊗——
−5° Isotherm : - - - ¦ - - -
Dotted tie lines, Taylor, 25°.
Full tie lines, Sidgwick and Spurrell at 3°.

liquid phase appears; we have now reached the triple line, solid benzene–solution I–solution II (conveniently written S–L_1–L_2). This new liquid is the conjugate solution, the composition of which is given by the point *b*, which is at the other end of the tie-line *ab*; being in equilibrium with the first liquid, it must have the

same pressure of benzene vapour, and so must also freeze at 3°. Thus at 3° the L_1–L_2 part of the curve is confined to the part *ab*; at *b* the solid curve begins again, passing between the two-liquid curve and the side *AW*.

The triple line, that is, the curve joining the whole series of triple points S–L_1–L_2 for all mixtures of alcohol and water on addition of benzene, will begin on the line *BW* (no alcohol) at 5·39° (triple point, water–benzene liquid–benzene solid) at two points corresponding, respectively, with 99·97 and 0·092 per cent. of benzene. As successive quantities of alcohol are added, the temperature of the triple points will fall, but at any given temperature (not too low) there will be two triple points corresponding with two conjugate solutions joined by a tie-line; these points will move towards one another with a fall in temperature as the alcohol increases, but more rapidly from the water than from the benzene side (owing to the position of the tie-lines), until they finally meet at the plait-point, where the tie-lines vanish. The temperature of this point is the lowest at which two liquid phases made up of water, alcohol, and benzene can co-exist. Our results show that this temperature is +2·50°, and the composition of the liquid about 80 per cent. of benzene and 2 per cent. of water; at 25° Taylor found at the plait-point 80·2 per cent. of benzene.

At −5° no second liquid can exist. The solid benzene curve has the form of the outer dotted line; somewhere near the water end it must meet the ice-curve, which at −5° starts on *AW* at 91 per cent. of water, but the solubility of benzene in this region is so small that it could not be investigated.

One point of practical importance may be mentioned, in view of the use of these mixtures for motor fuel. If a fourth component (another hydrocarbon) were added, the freezing point of the benzene would be proportionately lowered (some 5° for 10 per cent.), but if a paraffin were used for this purpose, it would certainly increase the tendency of the liquid to separate into two layers. The solubility of paraffins in alcohol containing water is extraordinarily small. The system hexane–alcohol–water has been examined at 0° by Bonner (*loc. cit.*, p. 777); the heterogeneous area occupies nearly the whole triangle. For example, whilst 90 per cent. aqueous alcohol will dissolve up to four times its weight of benzene, it will only dissolve a third of its weight of hexane.

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CLIII.—*The Catalytic Action of Iodine in Sulphonation. Part I.*

By JÑANENDRA NATH RÂY and MANIK LAL DEY.

THE present investigation was undertaken with the view of ascertaining whether the addition of a trace of iodine to sulphuric acid (D 1·84) facilitates the sulphonation of aromatic compounds (compare Heinemann, Brit. Pat. 12260 of 1915). It has been found that ordinary sulphuric acid and a trace of iodine can advantageously be used in place of fuming sulphuric acid with or without the addition of phosphoric oxide, etc. The nature of the product is changed in certain cases, thus making easy the preparation of some of the acids difficult to obtain. The catalytic sulphonation is facilitated by the presence of an amino-, hydroxy-, or halogen group in the molecule, but proceeds with less ease in the case of carboxylic acids, and is inhibited in the case of nitro-compounds. This fact probably explains the non-formation of disulphonic acids in the product. It is significant that there is an optimum temperature for each reaction in which maximum transformation takes place. It has also been noticed that there is some liberation of iodine vapour, but no trace of sulphur dioxide or hydrogen iodide could be detected in the space above the reaction mixture.

The discrepancy between the actual yield and that theoretically possible was accounted for in nearly all cases by the unchanged original material.

EXPERIMENTAL.

In the experiments to be described below, the general method of work was to heat a mixture of a few grams of the substance and the calculated quantity, or an excess, of sulphuric acid (D 1·84), together with a trace of iodine, for a few hours at the temperature, determined by trial, at which the transformation was greatest. The product was poured into water, the free sulphuric acid removed with barium carbonate or hydroxide, and the acid liberated from the filtrate by exactly neutralising with sulphuric acid. The solution of the free acid was concentrated, whereupon it was obtained in a crystalline condition. In some cases the product was poured into a saturated solution of potassium chloride, when the potassium salt separated in fine crystals (*o*-nitrophenol, etc.). The acid or the potassium salt was converted by the usual method into the sulphonyl chloride,

from which the amide, mercaptan, etc., were prepared in order to characterise it. Some of the sulphonic acids described gave colour reactions with ferric chloride and characteristic salts with heavy metals. When the acid could not be satisfactorily identified, it was transformed through its amino- or nitro-groups, etc., into the corresponding hydroxy- or amido-compounds, etc., in order to establish its constitution. In some cases it was found convenient to extract the sulphonic acid from the sulphonated mass with alcohol (*o*-toluidine).

The results obtained from the fusion of the products with potassium hydroxide were not taken into account unless substantiated by further evidence.

Sulphonation of Benzoic Acid.

A mixture of 12 grams of benzoic acid, 9 c.c. of sulphuric acid, and a small crystal of iodine was heated at 175—180° for about six hours, at the end of which time no free benzoic acid separated on diluting a sample. The liquid, after cooling, was poured into water, when a clear solution was obtained. The solution was neutralised with barium carbonate, the precipitated barium sulphate filtered off, and the filtrate exactly neutralised with dilute sulphuric acid. After filtering, the liquid was concentrated to a syrup, and, on keeping in a desiccator, crystals were obtained, which were drained, washed with a small quantity of alcohol, and dried over sulphuric acid in a vacuum. The anhydrous crystals melted at 134—135° (uncorr.), and were very hygroscopic.

A test experiment was conducted side by side with the above in which no iodine was used; almost the whole of the benzoic acid was recovered unchanged.

The crystals in aqueous solution gave a reddish-brown coloration with ferric chloride, but no precipitate, and were identified as *o*-sulphobenzoic acid by the formation of salicylic acid when fused with potassium hydroxide at a moderately low temperature (Found: $S=15 \cdot 0$. Calc. for acid $+ 1H_2O$: $S=14 \cdot 57$ per cent.).

In the above experiment, about a gram of benzoic acid sublimed away, and was thus not sulphonated.

The following table gives a résumé of the results obtained with other substances:

Substance.	Products by known methods.	By the present method.	Yield. Per cent.	Optimum temperature.	Time of reaction Hours.
Toluene	*o*- and *p*-acids	*p*-acid only	90–95	100°	1
Benzoic acid	*m*- and *p*-acids	*o*-acid	Above 95	175–190	6
Phthalic acid	—	no product	—	—	—
Catechol	3-acid	4-acid	75	50–55	1½
Quinol	mono- and di-sulphonic acids	mono-acid	73	70	4
o-Nitrophenol......	*p*-acid	*p*-acid	70	120	5
p-Nitrophenol	*o*-acid	*o*-acid	50	100–105	5
Nitrobenzene	—	no product	—	—	...
m-Dinitrobenzene ..	—	no product	—	...	—
o-Nitrotoluene	*p*-acid	*p*-acid	70	150	5
p-Nitrotoluene	*o*-acid	*o*-acid	5	140	4
o-Nitroaniline......	*p*-acid	*p*-acid	60	125	4½
p-Nitroaniline	*o*-acid	*o*-acid	50	140	3
3-Nitroaniline	6-acid	6-acid	10	150	4½
o-Toluidine	5-acid	5-acid	60–65	150	3
p-Toluidine........	—	no product	—	—	—
Chlorobenzene	*o*- and *p*-acid	*p*-acid	85	110	1½
Bromobenzene	*o*- and *p*-acid	*p*-acid	85	100	2

Summary and Conclusions.

(1) Iodine acts as a positive catalyst in sulphonation.

(2) Catalysis takes place smoothly when hydroxy-, amino-, chloro-, bromo-, or carboxy-groups are contained in the molecule, but with difficulty, or not at all, with nitro- or sulphonic substituents.

(3) There is an optimum temperature for each substance when the maximum transformation takes place.

We have much pleasure in according our best thanks to Sir P. C. Rây for the interest he has taken in the work.

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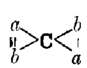
CLIV.—*The Resolution of the Keto-dilactone of Benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic Acid.*

By William Hobson Mills and Charles Reynolds Nodder.

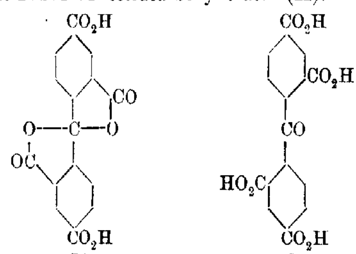
It follows from the theory of the tetrahedral distribution of the four valencies of the carbon atom that a *spiro*cyclic compound of the type



should exist in two enantiomorphous forms.

Previous attempts to obtain experimental confirmation of the molecular asymmetry of such compounds by resolution into optically active antipodes have, however, been unsuccessful (Marckwald, *Ber.*, 1906, **39**, 1176; Leuchs and various pupils, *Ber.*, 1912, **45**, 189, 2114; 1913, **46**, 2420), although Leuchs and Gieseler were able to obtain bis-δ-bromo-γ-valerolactone-αα-spirane, which contains only two asymmetric carbon atoms, in three inactive modifications, and they attributed the existence of the third form to the presence of a third centre of asymmetry in the substance, due to its *spiro*cyclic configuration.

A *spiro*cyclic compound of the type in question which appeared specially suitable for investigation is the keto-dilactone (I) of benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic acid (II).



(I.) (II.)

This compound was prepared by one of us (*Proc. Camb. Phil. Soc.*, 1915, **18**, 149) from di-*m*-xylyl ketone by oxidation to benzophenonetetracarboxylic acid, and dehydration of the latter by heating with hydrochloric acid. The method of synthesis, together with the fact that the product possesses the correct molecular weight, as we have found by the ebullioscopic method in acetone solution, leaves no doubt that it possesses the structure represented above.

After unsuccessful attempts with the commoner alkaloids, we have succeeded in resolving this substance into two optically active modifications with specific rotations $[\alpha]_D$ of approximately ±17° by means of a synthetic optically active base, α-phenylethylamine (Hunter and Kipping, T., 1903, **83**, 1147; Lovén, *J. pr. Chem.*, 1905, [ii], **72**, 307). Using the *d*-base, the *l*-acid was obtained, and the *d*-acid was isolated from the filtrate with the aid of the *l*-base.

The l-*Keto-dilactonic Acid.*—The following experiment is described as an example of several which have been carried out with similar results. The keto-dilactonic acid (5·75 grams) was suspended in methyl alcohol (100 c.c.), and a solution of *d*-α-phenylethylamine (4·09 grams), having $[\alpha]_D^{17}$ 39·64°, in methyl

alcohol (12 c.c.) was added drop by drop. The temperature rose from 22° to 26°, and a clear solution was obtained after the addition of about two-thirds of the base. After all the base had been introduced, dry ether (110 c.c.) was added. The salt rapidly crystallised, crystallisation being assisted by rubbing with a glass rod. The crop thus obtained (about 7 grams) was recrystallised from a mixture of methyl alcohol (210 c.c.) and ether (330 c.c.). The recrystallised salt (about 2 grams) was decomposed by treatment with hydrochloric acid (D 1·08), and the liberated keto-dilactonic acid carefully washed with water and dried. It was dissolved in methyl ethyl ketone, in which it is more readily soluble than in the other common solvents, and polarimetrically examined; 1·0375 grams in 30 c.c. gave α_D^{20} −2·25° (l=4), whence $[\alpha]_D^{20}$ −16·3°.

Of this product, 0·943 gram was combined, as before, with 0·671 gram of *d*-base. About 1 gram of salt was obtained, which, on decomposition, gave 0·6127 gram of acid. This was polarimetrically examined: 0·6127 in 13·1 c.c. gave $\alpha_D^{22\cdot5}$ −1·58° (l=2), whence $[\alpha]_D^{22\cdot5}$ −16·9°. The *l*-keto-dilactonic acid was recovered from solution and analysed (Found: C=59·4; H=2·44. $C_{17}H_8O_8$ requires C=59·99; H=2·37 per cent.).

The highest specific rotation which we have observed for the *l*-acid in the experiments which we have carried out up to the present is $[\alpha]_D^{20}$ −17·4° in methyl ethyl ketone solution.

The d-*Keto-lactonic Acid.*—The filtrate from which, as described above, the first crop of *d*-base–*l*-acid salt had been deposited gave, on acidification, 1·3 grams of an acid, which proved to be dextrorotatory; 0·679 gram in 30 c.c. of methyl ethyl ketone gave α_D^{21} 0·71° (l=4), whence $[\alpha]_D^{21}$ 7·9°. This acid was then combined with *l*-α-phenylethylamine, having $[\alpha]_D^{21}$ −38·5°, in the following manner. The acid (1·23 grams) was suspended in methyl alcohol (10 c.c.), *l*-base (0·87 gram) dissolved in methyl alcohol (2 c.c.) was added, and the salt precipitated with dry ether (6 c.c.). The acid (0·6585 gram) liberated from this salt was again combined with *l*-base (0·47 gram). The salt thus obtained gave, on decomposition, 0·559 gram of acid, which was polarimetrically examined; 0·559 gram in 13·1 c.c. gave α_D^{19} 1·50° (l=2), whence $[\alpha]_D^{19}$ 17·5°. From this acid, by repeating the above process, 0·426 gram of acid was obtained, on which the following observation was made: 0·426 gram in 13·1 c.c. of methyl ethyl ketone gave α_D^{19} 1·11°, whence $[\alpha]_D^{19}$ 17·1°. This acid was then recovered from solution and analysed (Found: C=59·70; H=2·38. $C_{17}H_8O_8$ requires C=59·99; H=2·37 per cent.).

The optically active forms of the keto-dilactonic acid are con-

siderably more readily soluble than the racemic form in all solvents examined. When saturated solutions of the *d*- and *l*-modifications in methyl ethyl ketone are mixed, an immediate, copious precipitate of the racemic form is produced.

To show the dependence of the optical activity on the lactonic structure of the compound, a solution of the *d*-acid in approximately 1 per cent. sodium hydrogen carbonate was examined in the polarimeter. The rotation was observed to diminish gradually, sinking to the half value in about twenty-four hours, and disappearing completely in about four days.

Further experiments on larger quantities of material are in progress in order to extend these observations, and particularly to determine the specific rotation of the optically pure acids.

One of us (C.R.N.) is indebted to the Department of Scientific and Industrial Research for a grant, for which he desires to express his thanks.

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CAMBRIDGE. [*Received, November 2nd,* 1920.]

CLV.—*The Preparation and Physical Properties of Carbonyl Chloride.*

By RALPH HALL ATKINSON, CHARLES THOMAS HEYCOCK, and WILLIAM JACKSON POPE.

ALTHOUGH carbonyl chloride, $COCl_2$, was discovered by John Davy in 1812 (*Phil. Trans.*, 1812, **102**, 144), and has found extensive scientific and technical applications, very little information is contained in the literature concerning its preparation and physical properties; Davy obtained the substance by effecting the combination of carbonic oxide and chlorine under the influence of sunlight, and this method of preparation was elaborated by Wilm and Wischin (*Annalen*, 1868, **147**, 150). Schutzenberger (*Bull. Soc. chim.*, 1869, [ii], **12**, 198) and Armstrong (*Proc. Roy. Soc.*, 1870, **18**, 504) prepared it by the action of sulphur trioxide on carbon tetrachloride; the latter method has been recently studied by Grignard and Urbain (*Compt. rend.*, 1919, **169**, 17), and used by Paternò and Mazzucchelli (*Gazzetta*, 1920, **50**, i, 30) in their determination of the physical properties of carbonyl chloride.

On the introduction of carbonyl chloride as a weapon of chemical

warfare, it became necessary to ascertain which method of preparation was most adaptable as a works process for manufacture, and one described by Paternò (*Gazzetta*, 1878, **8**, 233) presented itself as probably the best for this purpose. Paternò states that, on passing a rapid current of mixed carbonic oxide and chlorine at the ordinary temperature over animal charcoal, carbonyl chloride is produced very rapidly, with considerable evolution of heat.

Difficulties were encountered in carrying out the Paternò method of preparation; a number of samples of commercial animal and vegetable charcoals proved almost without effect as catalysts. Ultimately, a charcoal was prepared which gave quite remarkable results in inducing the combination of carbonic oxide and chlorine; this was made in the following manner. Fresh ox bones were crushed, embedded in sand in a clay crucible, and burnt in a muffle furnace; the residual charcoal was then well extracted with hot hydrochloric acid, washed with water, and heated, as before, in sand. Finally, the bone charcoal was kept at a red heat for some time in a current of dry chlorine.

The charcoal prepared in this way was crushed into small fragments, and, after sifting off the dust, 10 grams were filled into a U-tube immersed in a water-bath; a rapid current of mixed carbonic oxide and chlorine, in which the former was in rather the greater volume, was then passed over the charcoal. Carbonyl chloride was produced freely when the water-jacket was kept at the ordinary temperature, but, on raising the bath temperature to between 40° and 50°, combination proceeded at a greater rate than that at which it was possible to supply the mixed gases. Using the bone charcoal catalyst in the manner described, and liquefying the carbonyl chloride by means of a freezing mixture, about 10 kilograms of the compound were produced without any sign that the activity of the 10 grams of charcoal had suffered diminution.

It is thus shown that Paternò's method for preparing phosgene is correctly stated, but that certain precautions are necessary in the preparation of the animal charcoal used. Further investigations showed that certain kinds of vegetable charcoal act even more vigorously in inducing the condensation of carbonic oxide and chlorine, and the highly activated wood charcoal used in the Army box respirator proved more efficient as a catalyst than the bone charcoal described above. A U-tube containing 10 grams of the box-respirator charcoal, which had been heated in a current of chlorine gas, proved extremely efficient when the water-jacket was maintained at 14°, and one such tube kept at this temperature yielded more than 20 kilograms of carbonyl chloride, with no sign that the catalytic activity had diminished. In the work

subsequently described in this paper, this active vegetable charcoal was used.

The carbonic oxide required for laboratory work on the preparation of carbonyl chloride is conveniently prepared by passing carbon dioxide over red-hot coke contained in iron tubes heated in an ordinary combustion furnace; the resultant gas, after passing over slaked lime and drying over sulphuric acid, is practically pure carbonic oxide. In industrial operations, it is to be expected, however, that the available carbonic oxide will contain hydrogen. It thus becomes of importance to compare the reactivity of carbonic oxide and hydrogen with chlorine under the catalytic influence of charcoal.

A series of experiments was therefore arranged in which varying proportions of hydrogen were mixed with the carbonic oxide and chlorine passed over the catalyst. It was found that the vegetable charcoal was so active at 14° in inducing the combination of carbonic oxide and chlorine that no advantage accrued from heating it to 90°, and that, working at temperatures below 70°, no hydrogen chloride was produced; at 80°, a small proportion of hydrogen chloride was formed, and this was greatly increased at 90°. It is thus shown that an active form of charcoal will effect the complete conversion of a mixture of carbonic oxide and chlorine into carbonyl chloride at a temperature 50° below that at which it begins to exhibit catalytic activity towards a mixture of hydrogen and chlorine. This conclusion seems of importance in connexion with the manufacture of carbonyl chloride from carbonic oxide containing hydrogen.

Carbonyl chloride dissociates into carbonic oxide and chlorine at moderately high temperatures; Bodenstein and Dunant (*Zeitsch. physikal. Chem.*, 1908, **61**, 437) state that under atmospheric pressure carbonyl chloride dissociates to the extent of 67, 80, and 91 per cent. at 503°, 553°, and 603°, respectively, and that dissociation is complete at 800°. The results obtained by these observers indicate that carbonyl chloride is appreciably dissociated at 300°.

A little consideration will show that if carbonyl chloride free from chlorine is to be manufactured from a mixture of carbonic oxide and chlorine containing an excess by volume of the former, the temperature of the catalyst must be maintained below that at which carbonyl chloride suffers appreciable dissociation. Further, it may be anticipated that, within the dissociation range of temperature, the catalyst will act comparatively sluggishly; the chlorine content of the produced carbonyl chloride should thus be higher than that indicated by the equilibrium composition, and the

catalyst would become feebler with prolonged use. The following experiments were made for the purpose of further elucidating this question.

A mixture of chlorine and carbon monoxide, containing 2·5 per cent. excess by volume of the latter and standing over brine saturated with chlorine, was dried over sulphuric acid and calcium chloride and passed over the absorbent charcoal, the latter being contained in a glass tube 45 cm. in length and 1·9 cm. in diameter, at different temperatures. For temperatures from 20° to 150°, the tube was heated in an oil-bath; for temperatures from 150° to 520° the tube was wrapped in three layers of copper gauze, encased in heavy iron gas pipe, and heated in a gas furnace, the gas pressure being carefully regulated. A quill tube was fitted into the axis of the catalyser tube, so that the temperature at any point could be measured by a copper–constantan thermo-couple. Control experiments showed that, on sliding the thermo-couple along the tube, the maximum temperature variation from place to place and for a period of several hours was not more than 10° when no chemical action was occurring. With this arrangement of apparatus, it proved easy to obtain carbonyl chloride free from chlorine at temperatures between 50° and 200°, and to collect 90 to 97 per cent. of the theoretical yield of phosgene. The important point was established, however, that the major part of the combination took place at the position in the tube first exposed to contact of the mixed gases. This was further demonstrated by keeping the first, or entrance, half of the tube at 18°, and the second, or exit, half of the tube at 100°; the main disengagement of heat occurred at the junction between the cool and the hot charcoal. By sliding the thermo-couple along the tube, the heating effect of the reaction could be followed as the couple was passed along the tube from the front of the exit half to the front of the entrance half.

It would be expected that, on subjecting mixtures of carbon monoxide and chlorine to the action of the catalyst, a certain maximum temperature would be attained which could not be exceeded—the equilibrium temperature at which the reverse action absorbed the heat liberated. On passing the mixed gases at the rates of 0·84 and 2·4 litres per minute, the temperature of 464° was attained, and remained constant; this is to be regarded as the maximum temperature which can be attained in the large-scale catalysing vessels used in the manufacture of carbonyl chloride. In the experiments just described, it is noteworthy that at the rate of flow of 0·84 litre per minute, the layer of charcoal found to be at 464° was only about 3 mm. long, whilst when the gas

passed through at 2·4 litres per minute, the layer of catalyst maintained at 464° was some 10 mm. in thickness. Attempts to prepare carbonyl bromide with the aid of charcoal as a catalyst were unsuccessful.

The Dissociation of Carbonyl Chloride.

Since the combination of carbon monoxide and chlorine is highly exothermic, $CO + Cl_2 = COCl_2 + 26C$, and the catalyst used is very active, it seemed undesirable to attempt the investigation of the dissociation curve of carbonyl chloride by the study of the association; the foregoing experiments have shown the difficulty of maintaining the catalyst at an even temperature during the formation of the chloride. A series of experiments was therefore made on the dissociation of carbonyl chloride for the purpose of determining the equilibrium between it and its dissociation products with temperature at the atmospheric pressure. Since the dissociation is endothermic and must proceed to equilibrium in contact with the catalyst, it should be possible to ensure that the catalyst will be kept at an even temperature, and will set up equilibrium at that temperature.

The carbonyl chloride used in all the further work described below was prepared from carbon monoxide and chlorine, and preserved in glass vessels in contact with mercury to ensure its freedom from chlorine.

The absorbent charcoal was maintained at a constant temperature, as described above, and a slow, steady stream of dry carbonyl chloride was passed over it. The gaseous products were passed through a separating funnel, *A*, of 338 c.c. capacity, entering at the bottom and leaving through a side-arm in the shoulder; when all the air had been displaced from *A*, the two taps were closed and a 20 per cent. potassium iodide solution was run in from a dropping funnel, *B*, stoppered into the neck of *A*. After well shaking the whole apparatus, further quantities of potassium iodide solution were run in until action was at an end. The solution was then washed out with water and the iodine titrated against thiosulphate in order to determine the free chlorine present in the gas. The residual gas, consisting of carbon monoxide with some carbonyl chloride and usually a little air, was passed into a gas pipette and shaken with sodium hydroxide solution to remove the chloride. The carbon monoxide was determined by absorption in a hydrochloric acid solution of cuprous chloride; the residual air was measured, and its volume deducted from the volume of the cylinder, *A*. Direct determinations of the chlorine, carbon monoxide, and

carbonyl chloride are thus obtained; the volumes of carbon monoxide and chlorine always corresponded closely, and in table I, which summarises the results, the mean of the two slightly differing volumes is given.

The degree of dissociation, D, of the carbonyl chloride is calculated from the formula

$$D = \frac{100 \times \text{Volume of } Cl_2}{\text{Volume of } COCl_2 + Cl_2},$$

and the curve (Fig. 1) is drawn by plotting the values of D against the temperature.

TABLE I.

Dissociation of Carbonyl Chloride.

		Percentage by weight.			Volume per cent.		Degree of dissociation,
	T°.	$COCl_2$.	Cl_2.	CO.	$COCl_2$.	CO & Cl_2.	D.
1......	101	99·54	0·32	0·13	99·10	0·45	0·45
2......	102	99·50	0·36	0·14	99·01	0·50	0·50
3......	151	99·50	0·36	0·14	99·01	0·50	0·50
4......	153	99·46	0·38	0·15	99·95	0·53	0·53
5......	208	99·16	0·60	0·24	98·36	0·82	0·83
6......	211	99·26	0·53	0·21	98·55	0·73	0·74
7......	237	98·68	0·94	0·37	97·41	1·30	1·32
8......	239·5	98·86	0·82	0·33	97·74	1·13	1·14
9......	309	94·38	4·02	1·59	89·38	5·31	5·61
10......	314	94·51	3·94	1·55	89·61	5·20	5·48
11......	318	94·37	4·03	1·59	89·34	5·33	5·63
12......	341	92·48	5·38	2·14	68·05	6·98	7·50
13......	400	78·62	15·34	6·04	64·79	17·60	21·36
14......	406	82·56	12·50	4·94	70·31	14·84	17·43
15......	443	68·89	22·31	8·80	52·57	23·71	31·08
16......	449	66·60	23·90	9·40	49·23	25·39	34·02
17......	460	64·05	25·78	10·17	47·14	26·43	35·92
18......	486	58·32	29·89	11·79	41·19	29·41	41·65
19......	505	66·51	24·02	9·47	49·85	25·08	33·47
20......	505	46·77	38·17	15·05	30·55	34·72	53·19
21......	506	72·48	19·74	7·78	56·87	21·57	27·50
22......	517	70·54	21·13	8·33	54·51	22·75	29·45

The method of experimentation which has been applied has the fault that it does not ensure the dissociation products being cooled so rapidly that their partial recombination is prevented. The effect of this is seen in the fact that certain points, namely, those from experiments numbered 19, 21, and 22, lie off the general course of the graph; in these experiments, the gas current was passed much more slowly than in the others. In consequence, it may be found later that the degree of dissociation for any particular temperature, as now recorded, is too low.

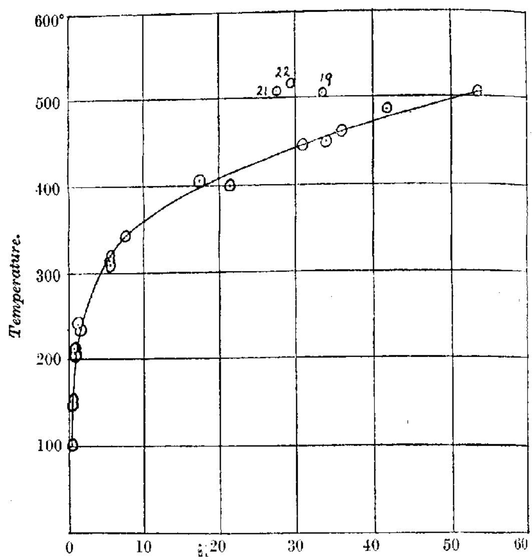
For practical purposes, it may be concluded that experiments 1 to 4, referring to temperatures of 100° to 150°, have given

identical results; the results of experiments 5 and 6, made at temperatures just above 200°, show a distinct increase in the degree of dissociation indicated at 100° and 150°. This increase is still more marked at 237° and 239°.

The accuracy of the suggestion made above, that carbonyl chloride free from chlorine can only be produced at temperatures

FIG. 1.

Dissociation of carbonyl chloride.



below 200°, must be regarded as fully substantiated by the above experimental results.

It is noteworthy that dissociation is indicated as occurring, even at 100° and 150°, by the results now recorded. It will be seen, however, that no difference is observable between the degree of dissociation indicated at 100° and 150°; the indication may therefore be attributed to some other cause than that of dissociation possibly to the slight reaction between potassium iodide in the acid solution and carbonyl chloride referred to below. Such a reaction would not disturb the equal volume ratio found between

the carbon monoxide and chlorine, and it is recorded by Besson (*Compt. rend.*, 1896, **122**, 140) that carbonyl chloride dissolves hydriodic acid, with liberation of iodine.

Whilst Bodenstein and Dunant (*loc. cit.*) found that carbonyl chloride is dissociated to the extent of 67 per cent. at 503°, the smoothed curve (Fig. 1) expressing the Cambridge results indicates the dissociation to be 55 to 56 per cent. at this temperature. The former workers analysed the mixture of gases by bubbling it through aqueous potassium iodide solution, and it is known that pure carbonyl chloride liberates a small amount of iodine in such a solution, and that the quantity of iodine formed increases on keeping (Delépine and Ville, *Bull. Soc. chim.*, 1920, [iv], **27**, 283). It is significant that Bodenstein and Dunant obtained higher values for the dissociation in those experiments which lasted the longest (45, 80, and 120 minutes), and that the dissociation-temperature curve plotted from their results slopes at an improbable angle. The heat of formation of gaseous carbonyl chloride, calculated from the degree of dissociation, is +25·4 C. at 475° and +23·4 C. at 425°, according to the Cambridge results, and +19·2 C. at 528° and +26·6 C. at 578°, calculated from the results of Bodenstein and Dunant. Thomsen ("Thermochemische Untersuchungen," 1882, II, 364; *Ber.*, 1883, **16**, 2619) gives the value +26·14 C. at the ordinary temperature, and criticises adversely the value +18·8 C. previously obtained by Berthelot.

Vapour Pressure of Carbonyl Chloride between −100° *and* +100°.

The boiling point of carbonyl chloride is given by Beckmann (*Zeitsch. anorg. Chem.*, 1907, **55**, 370) as 8·2°/756 mm.; no other data concerning the vapour pressure of this compound were available before the recent publication of Paternò and Mazzucchelli (*loc. cit.*), who made a series of determinations at temperatures between −19° and +24°. We have determined the vapour pressure at temperatures from −183° to +18° in one type of apparatus, and by means of another have extended the results up to +100°.

The apparatus used in the determination of the vapour pressure between −183° and +18° is depicted diagrammatically in Fig. 2. The distillation flask, *F*, of about 60 c.c. capacity, is connected with a differential manometer, *HB*, placed in front of a silvered mirror on which a millimetre scale is engraved, so as to avoid parallax. Through the neck of the flask passes a thistle funnel, *S*, for the purpose of sealing the leads of the thermo-couple air-tight by means of Faraday wax at the point where the bulb joins

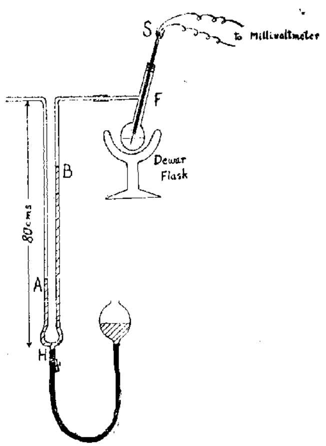
the stem. A joint thus made was found to be very satisfactory and quite unattacked by carbonyl chloride vapour.

The thermo-couple used was of copper–constantan; one junction was kept in ice and the other in the liquid carbonyl chloride. The couple was connected to a delicate millivoltmeter, which could be read with accuracy to 0·01 millivolt. For the graduation of the couple, the following temperatures were assumed:

TABLE II.

		Millivolts.
Steam at 760 mm. pressure	100°	+4·07
Melting ice	—	0·00
Freezing point of mercury	−39	−1·38
Solid carbon dioxide and ether	−79	−2·65
Boiling liquid oxygen	−183	−5·12

FIG. 2.



The millivolts corresponding with each of these temperatures were read off on the instrument, and the results plotted. The accuracy of the calibration was confirmed by determining with the aid of the couple the boiling point of a very pure sample of ethylene; this gave the value −104°, which compares well with the standard value of −103·5° given by Wroblewski and Witkowski.

After some preliminary trials, the following procedure was adopted. About 50 c.c. of pure liquid carbonyl chloride was distilled into the flask, *F*; the mercury was then run out of the mano-

meter, and the whole apparatus exhausted while the contents of the flask were maintained at $-80°$. The temperature of the carbonyl chloride was then allowed to rise until vapour was freely given off. This process was repeated several times during the three days occupied by the experiments, so as to ensure the complete absence of air.

A series of observations of the pressure and temperature of the carbonyl chloride was made at the selected temperatures, with the following results (table III):

TABLE III.

	Temperature.	Pressure mm. of Hg.
Water-bath	$+100°$	16.07×760
,, ,,	$+50$	5.11×760
,, ,,	$+17.5$	1105·5
Melting ice	—	568·3
Ice and salt mixture	-19	236·0
Freezing point of mercury	-39	89·5
Solid carbon dioxide and ether	-79	4·0
Boiling liquid oxygen	-183	0 mm.

These results have been plotted on the curve (Fig. 3), from which the vapour pressures of carbonyl chloride for each 10° between $+20°$ and $-100°$ have been taken; these values are included in table V.

After the vapour pressure of carbonyl chloride had been measured over the range $-183°$ to $+18°$, recourse was had to a different form of apparatus in order to extend the observations up to 100°. A sealed tube containing carbonyl chloride and a special type of manometer was heated in a water-bath to the desired temperature, and kept there for two to three hours. The glass manometer is shown in Fig. 4. The graduated tube, AB, was carefully calibrated by means of mercury. At the same time, the volume of the manometer was measured by weighing the amount of mercury which it contained. After the manometer had been thoroughly cleaned, the tube, AB, was silvered internally. The slight difference in the weight of the manometer before and after silvering proved that the amount of silver deposited was so small that its effect could be neglected.

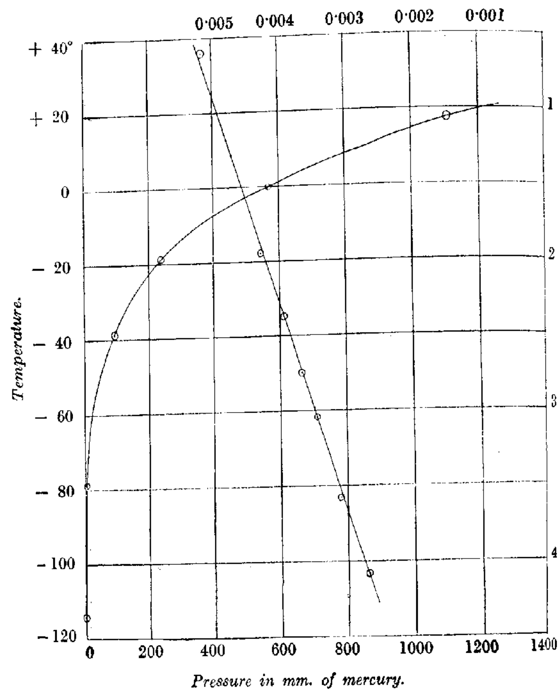
The manometer, having been carefully cleaned and dried, was filled with dry air and lowered into a hard glass tube containing about 10 c.c. of dry mercury (see Fig. 5). A wire, W, served to keep the manometer upright in the centre of the tube. The tube was drawn off, and finally sealed after 30 c.c. of pure liquid carbonyl chloride had been introduced in the usual manner; due care was taken to ensure that the space above the liquid contained

carbonyl chloride vapour only, and that air was absent. The pressure tube, placed inside an iron tube, was kept at 50° for two hours in a water-bath.

As the pressure of the vapour increases, it forces the mercury into the manometer, thereby compressing the air. When the

FIG. 3.

Vapour pressure of carbonyl chloride.



mercury rises into the silvered part of the tube, it dissolves the silver as far as the highest point it reaches. Thus a record is made of the volume of the compressed air at the temperature of the experiment.

After the tube had cooled and a note been made of the point to which the mercury had dissolved the silver, the experiment was

repeated at 100°. The following data were obtained: volume of manometer, 4·675 c.c.; barometer, 758 mm.; temperature, 16·6°. Volume of compressed air at 50° = 1·038 c.c., and at 100° = 0·380 c.c. The following results were calculated after applying corrections for the pressure of the columns of carbonyl chloride and mercury:

Vapour pressure of carbonyl chloride at 50° = 5·11 × 760 mm.
" " " " 100° = 16·07 × 760 mm.

It was noticed that the surface of the mercury was slightly dirty

FIG. 4.

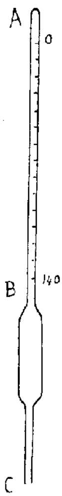


FIG. 5.

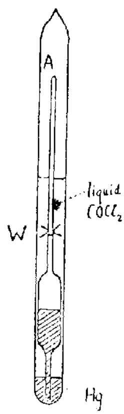
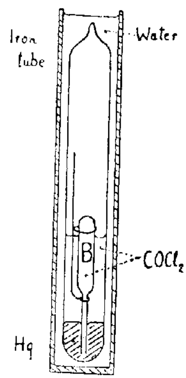


FIG. 6.



after these experiments; it is suggested that some chemical change occurs in accordance with the equation

$$2Hg + COCl_2 = CO + Hg_2Cl_2,$$

and that the two values last given may be rather high by reason of the formation of a trace of carbonic oxide.

From the vapour-pressure determinations now recorded, the molecular heat of evaporation (without performance of external work) of carbonyl chloride between 0° and 8° is calculated as approximately 5500 calories. A molecular heat of evaporation of 5500 calories for carbonyl chloride gives a value of 28° to 29° for the molecular rise in boiling point of this solvent; Beckmann (*Zeitsch. anorg. Chem.*, 1907, **55**, 371) has determined this

quantity experimentally as 29°. Since the latter value is obtained as the mean of six values lying between 27·2° and 30·8°, the agreement between his value and ours may be considered satisfactory.

Our values for the vapour pressure of carbonyl chloride at the higher temperature are rather higher than the Italian ones, whilst at 0° and below the reverse is the case. That our values are concordant among themselves is seen from the fact that the curve plotted between the reciprocal of the absolute temperature and the logarithm of the observed vapour pressure is practically a straight line; this curve is, indeed, drawn as a straight line in Fig. 3.

Since the vapour-pressure curve for carbonyl chloride only begins to fall rapidly at below −40°, it is clear that considerable losses will occur in the preparation unless the effluent gas saturated with carbonyl chloride is cooled well below −40°. The solubility of the chloride in a number of liquids, from which it might be subsequently recovered by evaporation, was therefore ascertained in order to learn whether washing the effluent gas with a solvent would lead to economy.

Solubility of Carbonyl Chloride in Organic Liquids.

Two or three c.c. of the solvent to be used are placed in a glass bulb of about 10 c.c. capacity immersed in a constant-temperature bath, and a slow current of the gas evolved from gently boiling carbonyl chloride is passed through the bulb until no further absorption occurs. Saturation was generally complete in about three hours, and the contents of the bulb were then hermetically sealed. The weight of the saturated solution was given by direct weighing, and the quantity of carbonyl chloride present determined by breaking the bulb in a closed bottle containing 50 or 100 c.c. of standard sodium hydroxide solution and titrating with standard acid. The number of grams of carbonyl chloride dissolved by 100 grams of solvent are now stated.

Toluene.—At 17·0°, 23·5°, 30·5°, and 31·5°: 244·7, 124·2, 79·38, and 74·48 respectively.

Coal-tar Xylene.—At 12·3°, 16·4°, 16·9°, 23·8°, and 29·8°: 457·3, 225·6, 217·9, 103·4, and 71·24 respectively.

Creosote Oil.—At 16·2°: 77·42.

Petroleum boiling at 180–280°.—At 12·3°, 15·8°, 16·7°, 22·4°, 23·7°, 29·9°, and 30°: 263·8, 163·1, 143·4, 79·5, 71·2, 49·2, and 48·6 respectively.

Heavy Lubricating Oil.—At 15·6°, 23·5°, and 31·0°: 79·7, 39·3, and 24·5 respectively.

Nitrobenzene.—106·4 at 16·8°.

a-Chloronaphthalene.—104·5 at 17·0°.

Chlorobenzene.—At 12·3°, 16·6°, 16·7°, 24·2°, and 29·7°: 422·1, 204·3, 221·6, 99·9, and 81·9 respectively.

Acetylene Tetrachloride.—At 16·8°, 25·1°, and 29·9°: 149·7, 89·4, and 74·9 respectively.

The solubility of carbonyl chloride differs widely according to the solvent. Toluene, coal-tar xylene, and chlorobenzene are by far the best solvents of those examined, and in view of their elevated boiling points would appear to offer most advantages as scrubbing agents for effluent gases containing carbonyl chloride. Ordinary burning petroleum boiling at 180° to 280° is the next best solvent, and heavy mineral lubricating oil and acetylene tetrachloride are not quite so good.

Melting and Freezing Points of Carbonyl Chloride.

The only recorded melting point for carbonyl chloride is that given by Erdmann (*Annalen*, 1908, **362**, 148) as −118°. Our determinations were made by immersing the bare junction of a standardised copper–constantan thermo-couple in pure liquid carbonyl chloride; on cooling in a bath of liquid air, the carbonyl chloride solidified to a white, crystalline mass, and on allowing the temperature to rise slowly, the temperature, as recorded by a milli-voltmeter, remained steady at −126° throughout the melting of the substance. On cooling the liquid very slowly, with constant shaking, the carbonyl chloride commenced to crystallise at −128°.

Density of Liquid Carbonyl Chloride.

The density of liquid carbonyl chloride was determined by Emmerling and Lengyel (*Annalen, Supp.*, 1870, **7**, 106) as 1·432 at 0°/4° and as 1·392 at 18·6°/4°; Paternò and Mazzucchelli (*loc. cit.*) have quite recently made a series of careful determinations between −15·4° and +59·9°. We have determined the density at −104·0°, −79°, 0°, and +49·9° with the aid of weight thermometers of transparent silica; two such thermometers, *A* and *B*, were used.

After filling the thermometers with mercury and repeatedly boiling out, they were cooled for some hours in ice, dried in a vacuum desiccator, and weighed, precautions being taken to collect the mercury overflow; thermometer *A* contained 80·1054 grams of mercury at 0°, whilst *B* contained 67·2640 grams. Assuming

Regnault's value of 13·5955 grams for the weight of 1 c.c. of mercury at 0°, the capacities of A and B are calculated as 5·8920 and 4·9475 c.c. respectively.

Thermometer A was filled with mercury at 0°, heated in a steam hypsometer (Bar. 768 mm.) for an hour, and then weighed; it contained 78·6835 grams of mercury at 100·3°. From these values, the coefficient of apparent expansion of mercury in silica is calculated as $(1·4219)/(78·6835 \times 100·3) = 0·000,180,17$; assuming Regnault's value of 0·000,180,92 for the coefficient of absolute expansion of mercury between 0° and 100°, the coefficient of cubic expansion of transparent silica becomes 0·000,000,75, a quantity which is small enough to be neglected.

In making the density determinations at 0° and lower temperatures, the thermometer A was filled with liquid carbonyl chloride in the ordinary way and kept at the steady, low temperature for for half to one hour; no attempt was made to weigh the vessel, on account of the difficulty of preventing moisture from the air condensing on it during transference. The weight of carbonyl chloride was found by removing the tube from the cooling bath and lowering it into a bottle containing 200 c.c. of ice-cold standard (2N) sodium hydroxide, which was then stoppered and clamped. The liquid in the thermometer slowly boiled off, usually taking from one to two hours, and when all had evaporated and reacted with the alkali, the excess of the latter was determined by titration with an acid; the weight of carbonyl chloride was then calculated.

In making the determination at +49·9°, the weight thermometer, B, was filled at −79°, and was then lowered, nose downwards, into a stout combustion tube, the lower end of which contained mercury. Cold carbonyl chloride was poured into the tube, which was then drawn off and placed inside an iron tube (see Fig. 6) gradually heated to 49·9° in a water-bath, and kept at that temperature for three hours. The tube was then slowly cooled, finally in ice and salt, and opened in the same way as in an ordinary pressure-tube experiment. The thermometer, which now contained mercury and carbonyl chloride, was withdrawn from the tube, drenched on the outside with cold ether, placed in the standard sodium hydroxide solution, and allowed to become warm slowly; the titration was then performed as before.

All errors due to the deformation of the silica tube by pressure were in this way eliminated, as the pressure within and without the tube was practically the same.

The density of carbonyl chloride (that is, weight in grams of 1 c.c.) was determined at −104° (boiling point of ethylene), −79° (solid carbon dioxide wetted with ether), 0° (ice), and +49·9°

(thermo-regulator); the results of the actual experiments are given in tabular form (table IV).

TABLE IV.

Temperature.	Weight thermometer.	Weight of $COCl_2$ in grams.	Density of $COCl_2$. (Weight of 1 c.c. of liquid.)
$-104.0°$	A (Vol. 5·892 c.c.)	9·892	1·679
-79	"	9·519	1·616
-79	"	9·503	1·613
0	"	8·463	1·436
0	"	8·443	1·433
$+49.9$	B (Vol. 4·948 c.c.)	6·502	1·314

From these results, a smooth curve was drawn, and a table (table V) constructed giving the density of carbonyl chloride for each 10° from $-100°$ to $+50°$.

TABLE V.

Density and Vapour Pressure of Liquid Carbonyl Chloride.

Temperature.	Density. Grams per c.c.	Vapour pressure. Mm. of mercury	Temperature.	Density. Grams per c.c.	Vapour pressure. Mm. of mercury.
$-110°$	1·685	—	-20	1·481	226
-100	1·663	—	-10	1·459	361
-90	1·640	—	0	1·435	568
-80	1·617	4	$+10$	1·412	844
-70	1·594	11	$+20$	1·388	1212
-60	1·572	24	$+30$	1·363	—
-50	1·549	47·5	$+40$	1·338	—
-40	1·526	85	$+50$	1·314	5.11×760
-30	1·504	141			

The mean coefficient of cubical expansion of carbonyl chloride between $-79°$ and $+49.9°$ is calculated as

$$(1.6145 - 1.3140)/(1.3140 \times 129) = 0.001,77.$$

The values for the temperature ranges $-104°$ to $-79°$, $-79°$ to 0°, and 0° to $+49.9°$ are 0·001,60, 0·001,59, and 0·001,84 respectively.

The values for the density of liquid carbonyl chloride which we now give are slightly higher than those obtained by the Italian workers; the latter obtained their product by the action of sulphur trioxide on carbon tetrachloride, and it is curious that Emmerling and Lengyel, who prepared their material, as we did, by the combination of carbonic oxide and chlorine, obtained results for the densities which are almost identical with ours for the two tempera-

tures at which they worked. The discrepancies between the results obtained by Paternò and Mazzucchelli and by ourselves may possibly be traced to the presence of some characteristic impurity in the carbonyl chloride made by one or the other method.

The work described in the present paper was carried out for the purposes of the Chemical Warfare Department, and permission for its publication has been given by the General Staff. Our thanks are due to our assistant, Mr. George Hall, for much help in experimental work.

The Chemical Laboratory,
University of Cambridge. [*Received, October 15th*, 1920.]

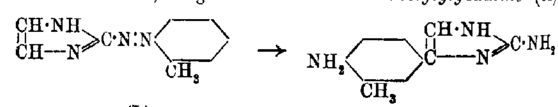
CLVI.—o- *and p-Tolueneazoglyoxalines.*

By Frank Lee Pyman and Leonard Allan Ravald.

In continuation of previous work on arylazoglyoxalines (Fargher and Pyman, T., 1919, **115**, 217), the interaction of *o*- and *p*-toluenediazonium chlorides and glyoxaline has been studied. The methods employed and the products obtained are generally similar to those described in the previous communication.

o-Toluenediazonium chloride combines with glyoxaline in aqueous sodium carbonate, giving 2-o-*tolueneazoglyoxaline* (I) in poor yield, a considerable amount of bis-*o*-tolueneazo-*o*-cresol being produced as a by-product. On replacing the sodium carbonate by sodium hydroxide, the yield was very little better, but the by-products were of different character, whilst when sodium hydrogen carbonate was used in the place of sodium carbonate, bis-*o*-tolueneazo-*o*-cresol was again produced, but no tolueneazoglyoxaline.

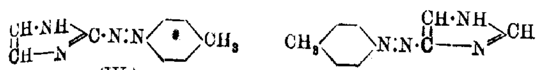
2-*o*-Tolueneazoglyoxaline resembles 2-benzeneazoglyoxaline closely in physical and chemical properties. On reduction with stannous chloride, it gives 2:4′-*diamino*-4-m-*tolylglyoxaline* (II).



(I.) (II.)

The combination of *p*-toluenediazonium chloride with glyoxaline in aqueous sodium carbonate leads to the formation of 2-p-*tolueneazoglyoxaline* (III) in good yield, together with a small amount

of an isomeride, doubtless 4-p-*tolueneazoglyoxaline* (IV), and a quantity of *p*-tolueneazo-*p*-cresol. We had expected that



(III.) (IV.)

2-*p*-tolueneazoglyoxaline would resemble 2-*p*-bromobenzeneazoglyoxaline in giving a good yield of 2-aminoglyoxaline when reduced with stannous chloride under the conditions employed by Fargher and Pyman (*loc. cit.*, p. 244), but this was not the case, 2-aminoglyoxaline being produced in a yield of less than 15 per cent. of the theoretical, together with *p*-toluidine, guanidine, ammonia, and unidentified products. When 2-*p*-tolueneazoglyoxaline is reduced with zinc dust and acetic acid under the conditions previously employed for the reduction of 2-benzeneazoglyoxaline (*ibid.*, p. 241), *p*-toluidine and glycocyamidine were obtained in yields amounting to 97 and 42 per cent. of the theoretical respectively.

EXPERIMENTAL.

2-o-*Tolueneazoglyoxaline.*

o-Toluidine (10·7 grams) was diazotised, and the product added to a solution of 6·8 grams of glyoxaline and 20 grams of anhydrous sodium carbonate in 500 c.c. of water at 5°. After keeping overnight, the brown deposit was collected and extracted with 5 per cent. hydrochloric acid. On the addition of sodium carbonate, the extract deposited 4·8 grams of crude 2-*o*-tolueneazoglyoxaline melting at 165°, the yield amounting to 26 per cent. of the theoretical. The material insoluble in dilute hydrochloric acid amounted to 7 grams and melted at 120°; after recrystallisation from alcohol, it gave 3·3 grams of pure bis-*o*-tolueneazo-*o*-cresol, which melted at 147° (corr.), and was identified by analysis [Found (mean): C=72·4; H=6·0; N=16·6. Calc.: C=72·2; H=6·1; N=16·9 per cent.] and by comparison with a specimen prepared by the action of *o*-toluenediazonium chloride on *o*-cresol (Noelting and Werner, *Ber.*, 1890, **23**, 3260).

2-o-*Tolueneazoglyoxaline* crystallises from alcohol in brownish-yellow crystals of indeterminate shape, which melt at 185—186° (corr.). It is very readily soluble in alcohol or chloroform, less readily so in ether or benzene (Found: C=64·6, 64·4; H=5·4, 5·7; N=30·1. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

Reduction of 2-o-Tolueneazoglyoxaline with Stannous Chloride. Isolation of 2:4′-Diamino-4-m-tolylglyoxaline.

Two grams of 2-*o*-tolueneazoglyoxaline were dissolved in 20 c.c. of hot 2·5 per cent. hydrochloric acid and mixed with 12 c.c. of stannous chloride (40 per cent. w/v) in hydrochloric acid. On cooling the solution and adding 20 c.c. of concentrated hydrochloric acid, 4 grams of a crystalline stannichloride were deposited, which, after the removal of the tin, gave 2 grams of 2:4′-diamino-4-*m*-tolylglyoxaline dihydrochloride, that is, 67 per cent. of the theoretical yield.

2:4′-*Diamino*-4-m-*tolylglyoxaline dihydrochloride* separates from dilute hydrochloric acid in microscopic needles, which form a white, spongy mass. After drying at 50°, it contains $1H_2O$. It is readily soluble in cold, very readily so in hot, water [Found (in substance dried at 50°): C=43·0; H=5·8; N=19·9, 20·1; Cl=25·7; H_2O=6·9. $C_{10}H_{12}N_4,2HCl,H_2O$ requires C=43·0; H=5·8; N=20·1; Cl=25·5; H_2O=6·5 per cent.].

Its reactions with potassium permanganate, sodium nitroprusside, sodium diazobenzene-*p*-sulphonate, and nitrous acid are similar to those of the lower homologue (T., 1919, **115**, 240). The base appears to be unstable, for, on the addition of ammonia to an aqueous solution of the dihydrochloride, a white, flocculent precipitate is formed, which rapidly darkens when separated from the solution.

The sparingly soluble *sulphate* separates as a mass of woolly needles on the addition of sulphuric acid to an aqueous solution of the salt.

The *dipicrate* separates as a crystalline powder, which melts at about 210° (corr.) after sintering earlier. It is sparingly soluble in boiling water.

2- and 4-p-Tolueneazoglyoxalines.

p-Toluidine (10·7 grams) was diazotised, and the product added to a solution of 6·8 grams of glyoxaline and 20 grams of anhydrous sodium carbonate in 500 c.c. of water at 5°. After keeping overnight, the yellowish-brown, insoluble product was collected and extracted with 5 per cent. hydrochloric acid. One gram of dark red, amorphous matter remained undissolved, and, on crystallisation from alcohol, yielded *p*-tolueneazo-*p*-cresol, which melted at 112° (corr.), and was identified by analysis (Found: C=73·7; H=6·8; N=12·5. Calc.: C=74·3; H=6·3; N=12·4 per cent.) and by comparison with a specimen prepared by the action of

p-toluenediazonium chloride on *p*-cresol (Noelting and Kohn, *Ber.*, 1884, **17**, 354). The hydrochloric acid extract was basified with sodium carbonate, and deposited 15·2 grams of the mixed tolueneazoglyoxalines melting at 220°, that is, 86 per cent. of the theoretical yield. On recrystallisation from alcohol, 11·6 grams of 2-*p*-tolueneazoglyoxaline were obtained in a pure state, and small crops of impure material. From the final filtrate, 4-*p*-tolueneazoglyoxaline was isolated in the form of its hydrochloride.

2-p-*Tolueneazoglyoxaline* crystallises from alcohol in yellow leaflets, which melt at 235° (corr.). It is soluble in boiling alcohol to the extent of rather less than 5 per cent. (Found: C=64·1, 64·4; H=5·6, 5·6; N=30·1. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

The hydrochloride was crystalline, but deliquescent.

4-p-*Tolueneazoglyoxaline*, prepared from the pure hydrochloride, crystallised from alcohol in yellow leaflets, which melted at 152° (corr.) (Found: C=63·9; H=5·5; N=31·0. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

The *hydrochloride* crystallises from dilute hydrochloric acid in fine, yellow needles forming a felted mass. The air-dried salt melts first at 76° (corr.), loses $2H_2O$ at about 117°, and melts again after darkening at 185° (corr.). It is very readily soluble in water [Found (in air-dried salt): Cl = 13·8; H_2O = 13·5. $C_{10}H_{10}N_4,HCl,2H_2O$ requires Cl=13·7; H_2O=13·9 per cent.].

We desire to thank the Salters' Institute of Industrial Chemistry for the grant of a fellowship, which has enabled one of us (L.A.R.) to take part in the investigation.

MUNICIPAL COLLEGE OF TECHNOLOGY,
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CLVII.—*The Sulphonation of Glyoxalines.*

By FRANK LEE PYMAN and LEONARD ALLAN RAVALD.

DIRECT sulphonation of glyoxalines has not been effected previously, but in two cases derivatives of glyoxaline-2-sulphonic acid have been prepared indirectly. Thus, Anschütz (*Annalen*, 1895, **284**, 18) obtained 4:5-diphenylglyoxaline-2-sulphonic acid by the oxidation of 2-thiol-4:5-diphenylglyoxaline, whilst salts of caffeine-8-sulphonic

acid are formed by the action of hot aqueous sulphites on 8-chlorocaffeine (D.R.-P. 74045).

In view of the stability and pronounced aromatic character of glyoxaline, it seemed probable that this base, like pyrazole and pyridine, would be susceptible to direct sulphonation, and this has proved to be the case, a *glyoxalinesulphonic acid* being obtained in good yield under suitable conditions. Presumably, sulphonation takes place in the 4-position, as does nitration (Fargher and Pyman, T., 1919, **115**, 217; Fargher, this vol., p. 668), and the investigation will be continued and extended to alkylglyoxalines to elucidate this point.

Experimental.

Glyoxaline, in the form of its sulphate, was added to sulphuric acid or fuming sulphuric acid and the mixture heated. The diluted solution was treated with barium hydroxide and subsequently with carbon dioxide, evaporated to dryness, and extracted with chloroform. This removed the unchanged glyoxaline and left crude barium glyoxalinesulphonate.

The consequences of varying the conditions appear in the following table:

No. of experiment.	Proportion of glyoxaline (base) to fuming sulphuric acid.	Strength of fuming sulphuric acid in percentage of free sulphur trioxide.	Temperature.	Duration of heating (hours).	Yield of sulphonate. Percentage of theoretical.	Glyoxaline recovered. Per cent.
1	1 : 2	(98% H_2SO_4)	100°	3	Nil.	85
2	1 : 3	12	,,	,,	Nil.	74
3	,,	40	,,	,,	4	96
4	,,	,,	160	,,	18·5	57
5	,,	,,	,,	6	9	69
6	,,	,,	200	3	11	85
7	,,	,,	260	,,	2	46
8	,,	50—60	100	,,	20	46
9	,,	,,	160	,,	52	Trace.
10	,,	,,	,,	,,	55	26
11	1 : 4	,,	,,	,,	78	Trace.
12	,,	,,	,,	,,	70	,,
13	,,	,,	,,	,,	83	,,

The crude barium glyoxalinesulphonate crystallised almost completely on treatment with water. From the pure salt the free acid and the sodium and ammonium salts were prepared by treatment with the equivalent quantities of sulphuric acid and its salts.

Glyoxalinesulphonic acid crystallises from water in large, colourless cubes which are anhydrous. It begins to soften at 290° and is

entirely molten at 307° (corr.). It is soluble in about 5 parts of cold or 2 parts of hot water, but is almost insoluble in alcohol. (Found, $C=24\cdot2$; $H=2\cdot6$; $N=18\cdot9$. $C_3H_4O_3N_2S$ requires $C=24\cdot3$; $H=2\cdot7$; $N=18\cdot9$ per cent.)

Glyoxalinesulphonic acid is strongly acid to litmus, whilst its salts are only faintly alkaline. It does not combine with strong aqueous acids. On adding sodium diazobenzene-*p*-sulphonate to glyoxalinesulphonic acid in excess of aqueous sodium carbonate, no immediate coloration is produced, but a deep red colour develops in the course of a few minutes. In the presence of sodium hydroxide the solution remains pale yellow even on keeping. An attempt to nitrate glyoxalinesulphonic acid by boiling 1·1 grams with a mixture of 1 c.c. of fuming nitric acid and 1 c.c. of sulphuric acid was unsuccessful, the glyoxalinesulphonic acid being recovered unchanged.

The *barium* salt crystallises from water in colourless octahedra, which are anhydrous, soluble in 3 parts of hot water, and little less soluble in cold water, but insoluble in alcohol. (Found: $Ba=34\cdot2$. $(C_3H_3O_3N_2S)_2Ba$ requires $Ba=34\cdot1$ per cent.)

The *sodium* salt crystallises from water in large, colourless tablets, which contain $2H_2O$. It is very readily soluble in water, but almost insoluble in alcohol. (Found, in air-dried salt: $Na=11\cdot2$; $H_2O=17\cdot7$. $C_3H_3O_3N_2SNa,2H_2O$ requires $Na=11\cdot2$; $H_2O=17\cdot5$ per cent.)

The *ammonium* salt crystallises from water in large, colourless prisms. It is very readily soluble in water, and easily so in hot moist alcohol, but almost insoluble in absolute alcohol. It loses ammonia at temperatures above 100°, leaving the free acid. The air-dried salt lost 1·5 per cent. of water in a vacuum over sulphuric acid. (Found, in salt dried in a vacuum: $N=25\cdot4$; loss at $120°=10\cdot5$. $C_3H_3O_3N_2S\cdot NH_4$ requires $N=25\cdot4$; loss of $NH_3=10\cdot3$ per cent.)

We desire to thank the Salters' Institute of Industrial Chemistry for the grant of a fellowship which has enabled one of us (L. A. R.) to take part in the investigation.

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CLVIII.—*The Velocity of Decomposition of High Explosives in a Vacuum. Part I.*

By ROBERT CROSBIE FARMER.

PREVIOUS work on the stability of explosives has been devoted almost entirely to the nitric esters. The methods used depend for the most part on the detection and estimation of the oxides of nitrogen evolved on heating, and are not, in general, applicable to nitro-aromatic compounds or to mercuric fulminate, azides, etc. In order to meet the need for a simple quantitative stability test for such compounds, the vacuum test described below was developed. This has been widely used for high explosives, more particularly for trinitrophenylmethylnitroamine. It has proved itself so simple in use after some thousands of tests that it may be of interest for the investigation of other reactions in which gases are evolved. Some measurements of the rate of decomposition in a vacuum have been made on guncotton (Obermüller, *Mitt. Berl. Bezirksver.*, 1904, **1**, 30; Dupré, *Ann. Rep. Insp. of Explosives*, 1903, 26; 1904, 28; 1905, 29; Hodgkinson and Coote, *Chem. News*, 1905, **91**, 194; Robertson and Napper, T., 1907, **91**, 764; Willcox, *J. Amer. Chem. Soc.*, 1907, **30**, 271; Pleus, *Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1910, **5**, 121), on silver oxalate (Hoitsema, *Zeitsch. physikal. Chem.*, 1896, **21**, 137), trinitrotoluene (Verola, *Mém. poud. Salp.*, 1911—1912, **16**, 40), and tetryl (Knowles, *J. Ind. Eng. Chem.*, 1920, **12**, 246). The methods described were not, however, convenient as standard tests for high explosives.

From measurements on a large number of explosives, it appears that these are in all cases subject to a gradual decomposition, with evolution of gas, at temperatures below their ignition points. The velocity decreases strongly as the temperature is lowered, but there can be little doubt that a very slow decomposition must occur even at the ordinary temperature.

As in the case of nitric esters (Farmer, this vol., p. 811), the decomposition is partly catalytic and partly non-catalytic; when catalytic influences are eliminated, the velocity sinks to a minimum. In many cases, the catalytic decomposition outweighs the intrinsic decomposition of the pure substance, and it is frequently difficult to purify the explosive to such a degree that the catalytic influences are completely removed. For the same reason, different preparations of the same substance often differ considerably in their rates of decomposition. Frequently the evolution of gas proceeds

with an acceleration due to autocatalysis, whilst in other cases it becomes slower after a time, owing to the decomposition and consequent elimination of impurities. In many cases the presence of moisture gives rise to very erratic results, and special steps are therefore taken to eliminate this influence. As a rule, the decomposition has been carried only to the extent of a small evolution of gas. The measurement of small volumes of gas has, it is true, the disadvantage that the measurements are more affected by traces of volatile matter, etc., but if the decomposition is carried further, the products formed are liable to have a very disturbing effect, and frequently a very rapid evolution of gas sets in.

The nitro-aromatic compounds are, in general, very much more stable than the nitric ester explosives. Whilst guncotton shows a marked decomposition in Will's test at 135° in four hours, and nitroglycerin at a lower temperature, the trinitrobenzene derivatives require, in general, temperatures of 140° to 180° in order to give readily measurable volumes of gas on heating for 100 hours. The dinitro-compounds show scarcely any measurable decomposition. The nitroamines, such as tetryl, on the other hand, are less stable, and decompose sufficiently rapidly for measurements at 120°.

In order to give an approximate idea of the relative stability, the temperatures may be calculated by extrapolation, at which the gas evolution amounts to 1 c.c. per gram in 100 hours:

Trinitrobenzene	190—195°
Trinitrophenol	150—155°
2 : 4 : 6-Trinitrotoluene	135—140°
2 : 3 : 4- "	135—140°
3 : 4 : 6- "	130—135°
Trinitrophenylmethylnitroamine	115—120°
Cellulose nitrate (N = 13 per cent)	Approx. 100°

Trinitrotoluenes gave 0·8 to 1·8 c.c. of gas per gram in 100 hours at 140°. The differences in velocity between different samples indicated the presence of traces of catalysts, although most of the samples were very pure. There was practically no parallelism between the melting point and stability. The rate of evolution showed no acceleration; hence no autocatalysis occurred within limits measured. From the results obtained, it is evident that pure trinitrotoluene could be kept indefinitely at the ordinary temperature, but the actual rate of decomposition cannot be ascertained by direct extrapolation, as the results obtained in the case of tetryl have shown that a great increase in stability occurs on passing from the molten to the solid condition.

The isomeric trinitrotoluenes which accompany the symmetrical compound in small proportion on nitration of toluene were also

examined. The commercial products contained impurities which decreased their stability. When these were removed by crystallisation, 2:3:4-trinitrotoluene showed about the same stability as the 2:4:6-isomeride, whilst 3:4:6-trinitrotoluene was somewhat less stable. The stability of 2:4:6-trinitrotoluene was not sensibly affected by the addition of 1 per cent. of the other pure isomerides, but 5 per cent. of the 3:4:6-isomeride caused a slight increase of velocity.

Mixtures of picric acid and trinitrotoluene showed a lower rate of decomposition at 140° than trinitrotoluene alone. This was somewhat surprising, since the general experience is that acids decrease the stability. It is possible that the trinitrotoluene exists as an equilibrium in which a small quantity of an *iso*nitro-compound is present, the latter being the cause of the instability observed. Picric acid might readily cause the *iso*nitro-compound to revert to the normal nitro-compound, thus increasing the stability.

As an example of an unsaturated substance, castor oil was mixed with trinitrotoluene and with picric acid, and the mixtures were tested. The castor oil depressed the stability very strongly in both cases.

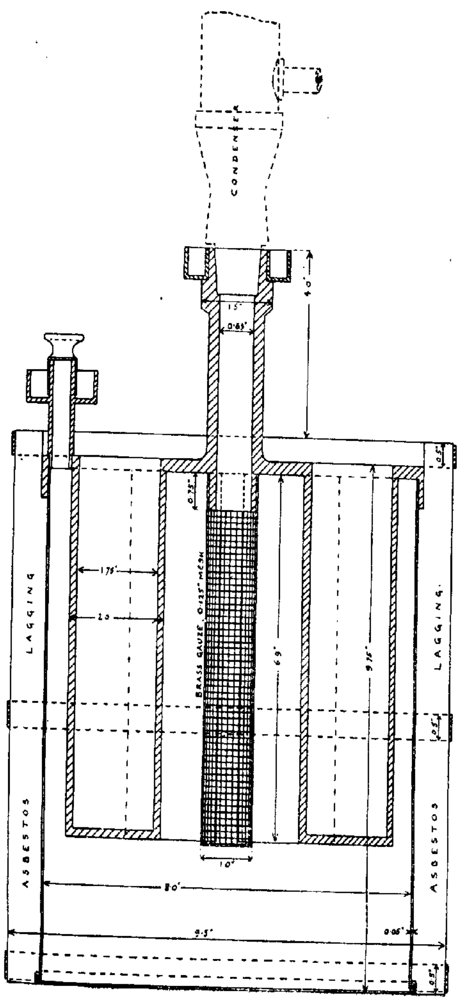
Trinitrophenol showed a stability intermediate between that of trinitrobenzene and that of trinitrotoluene. Trinitrobenzene showed extreme stability, even at the boiling point of aniline, and the stability was not perceptibly affected by wet and dry storage trials. This is of interest as showing that, notwithstanding the difficulty of introducing the third nitro-group, the trinitro-compound, when once prepared, is very stable.

EXPERIMENTAL.

Apparatus.—The thermostat (Fig. 1) consists of a cylindrical copper bath, which is maintained at the required temperature by a boiling liquid. The cover consists of a thin brass casting with six orifices for the heating tubes, and a short column to support the condenser. These all form part of the casting, thus avoiding joints, which are otherwise very apt to leak during protracted tests. The connexion with the condenser is made by a conical joint surmounted by a cap, which can be filled with vaselin or other material to lute the joint. The brass column also projects about 0·5 cm. into the interior of the bath, and is connected with a cylinder of coarse copper gauze of the same diameter as the tube and about 15 cm. in length. The object of this is to convey the condensed liquid down the centre of the bath and ensure uniform

heating. The lid has also a small opening for filling the bath. This is fitted with a cap and a cup for luting. A cylinder of lagging material surrounds the bath. The top of the bath is also

FIG. 1A.



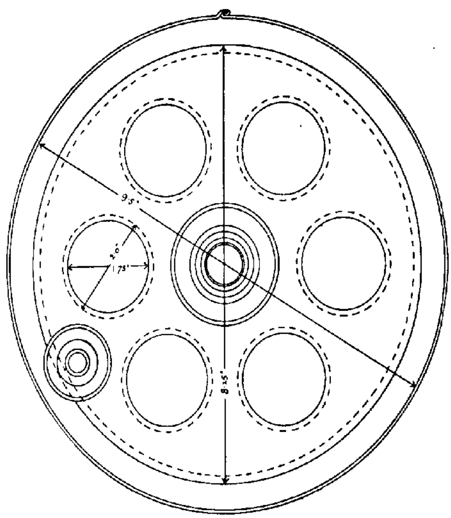
covered with a loose cake of asbestos lagging material about 3 cm. thick, with holes corresponding with those in the brass cover.

The condenser (Fig. 2) is of the multitubular pattern, and the water inlet tube is fitted with a funnel, as shown, so that the flow of water can be seen.

For temperatures from 80° to 100°, mixtures of alcohol and water were used. From 100° to about 135°, solutions of calcium chloride were generally taken. In the latter case, the addition of a little lime is advisable to avoid corrosion of the copper.

The temperature of the boiling calcium chloride solution is

FIG. 1B.

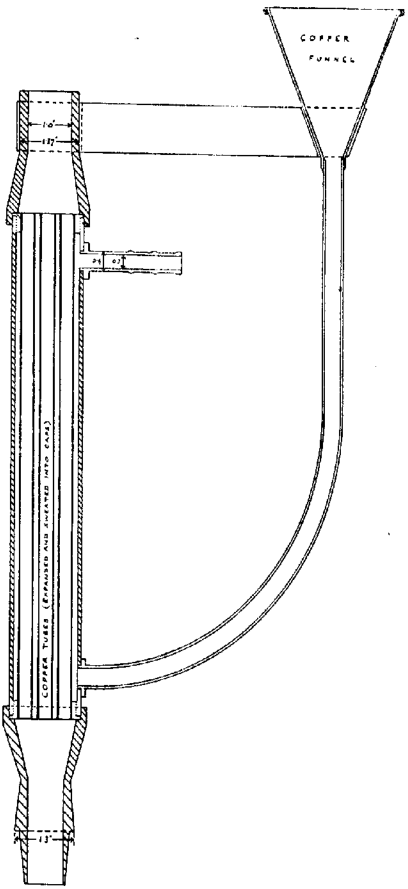


readily adjusted by adding water if too high, or by allowing water to evaporate if too low. The level of the liquid should be maintained at about 5 cm. from the lid of the bath.

Safety Precautions.—To guard against damage by explosion, steel tubes with closed bottoms were provided; these fitted loosely into the brass orifices, and were packed round with fine copper fillings to give good contact with the bath. They were made rather short (Fig. 3), since it was found that if they extended nearly to the surface of the bath, they became cooled by radiation, and irregular temperatures were obtained.

The thermostats were surrounded by screens and placed in a fire-proof shed. A cistern was provided to guard against failure of the water supply, and an automatic ball-cock tap was fitted to cut off the gas supply in case the cistern became empty.

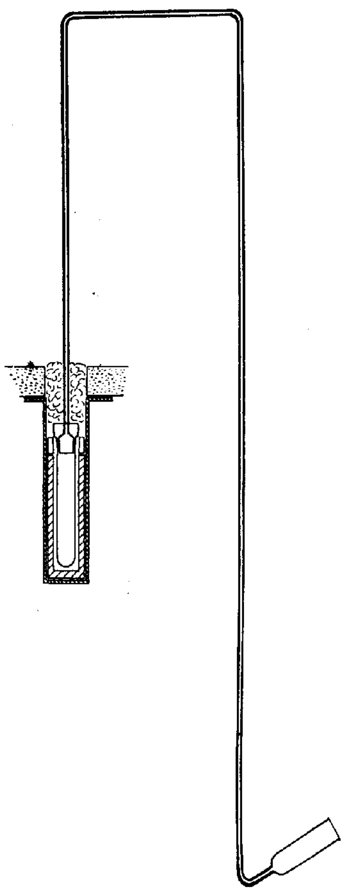
Fig. 2.



Heating Tubes.—The glass apparatus passed through numerous modifications in the course of a large number of measurements. The earlier patterns were fitted with glass taps for exhaustion, but it was found much better to avoid these, and the simple device shown in Fig. 3 was found to be a great improvement. In order to exhaust the tube, a quantity of mercury sufficient to fill the upright limb of the capillary tube is placed in the lower cup. This cup is connected with the pump by means of a rubber stopper. The apparatus is then inclined so that the cup is horizontal and the mercury lies in a pool in the cup, leaving a free passage between the pump and the capillary tube.

After exhaustion, the apparatus is returned to the upright position, and, on releasing the vacuum, the mercury rises in the capillary tube, which acts as a manometer during the test. The cup at the top of the heating tube is luted with mercury, and the apparatus is then ready to be transferred to the thermostat. It is important that the stopper be very well ground, and lubricated as thinly as possible with a non-reactive lubricant.

FIG. 3.



The thermometer is embedded in sand in a similar heating tube, which is introduced into one of the steel tubes and placed in the bath. Accuracy of the temperature readings is of great importance in view of the high temperature-coefficients of the decompositions.

Method of Working.—Very thorough cleaning of the apparatus is necessary, as traces of foreign matter have a marked catalytic effect. The tubes were cleaned successively with acetone, benzene, and hot chromic acid, and were then subjected to prolonged washing with water. The manometers were similarly cleansed. The complete removal of moisture is also of importance, since this frequently gives rise to abnormal accelerations. The explosive is dried at a temperature well below its decomposition point, and weighed quantities are introduced into the test-tubes. These are

then connected with the capillary tubes, the ground stoppers being thinly lubricated. The apparatus is then exhausted to about 5 mm. of mercury by means of a Geryk pump, and is heated to a temperature at which no measurable decomposition will occur (generally 80°) for some hours to remove water.

The apparatus is then again exhausted, dry air is allowed to enter through a three-way cock attached to the pump, and removed once more by the pump, and the apparatus is inserted in the thermostat. A little asbestos wool is packed round the stopper.

The time at which the heating commences is noted, and an arbitrary period is allowed to permit the pressure to settle down before the first reading is taken. This is necessary, on account of minute traces of residual volatile matter, and in some cases the volatility of the compound itself. In general, one and a-half hours have been found sufficient. The height of the mercury column is then read at intervals, in comparison with the barometric height. It is convenient to use, as barometer, a similar tube exhausted and placed near the apparatus. This automatically corrects the reading for temperature of the mercury and capillary depression.

To avoid differences in the level of the mercury in the lower cup, it is convenient to fill this up, so that it overflows into a dish as the mercury descends in the capillary tube.

In taking a number of readings, a sliding scale may be used with advantage. The zero is set to the mercury level in the barometer, and the difference between manometer and barometer can then be read off directly.

Calculation of Gas Volume.—The calibration of the apparatus includes measurements of the volume of the test-tube, the volume of unit length of the capillary, and the total length of the three limbs of the capillary tube from the stopper to a point on the capillary-tube level with the average height of mercury in the cup. The volume of explosive is deducted from the volume of the heating tube to obtain the net volume.

In calculating repeated readings with the same explosive and the same bath temperature, the following shortened method of calculation is useful: The bath temperature is practically constant; the ordinary temperature alters somewhat, but as this only affects the correction of the volume in the capillary tube, it may also be taken as constant (it was, in general, about 30°).

If the difference between barometer and manometer reading be p mm., the corrected volume of gas in the heating tube is equal to:

$$\text{Net gas space} \times \frac{273}{273 + \text{bath temp.}} \times \frac{p}{760}.$$

The corrected volume of gas in the capillary tube is equal to (total length $-760+p) \times$ (vol. of 1 mm.) $\times \frac{273}{303} \times \frac{p}{760} = p$ (total length $-760) \times$ (vol. of 1 mm.) $\times \frac{1}{843} + p^2$ (vol. of 1 mm.) $\times \frac{1}{843}$.

Hence the corrected volume is equal to

$$p\,(a+b)+p^2c,$$

where $a = \dfrac{\text{net gas space} \times 273}{760\,(273 + \text{bath temp.})}$;

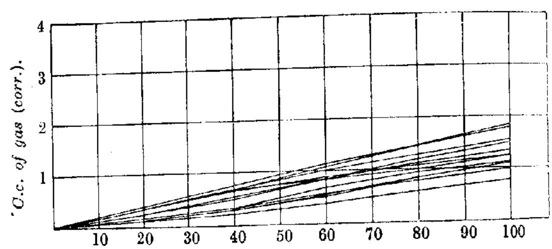
$$b = \frac{1}{843}\ (\text{length of capillary tube} - 760) \times (\text{vol. of 1 mm.})$$

$$c = \frac{1}{843}\ (\text{vol. of 1 mm.}).$$

These constants can be determined for the whole series of measurements, and the calculation is then very simple. The constants b and c depend only on the calibration of the apparatus; a depends also on the volume of explosive and the bath temperature.

Correction for Fluctuations in Bath Temperature.—The fluctuations due to alteration of boiling point with variations of the barometric pressure are of importance, as the velocity of decomposition usually increases approximately 100 per cent. for each 5 degrees, or 15 per cent. per degree. It is better to apply the correction to the time readings rather than to correct the

FIG. 4.



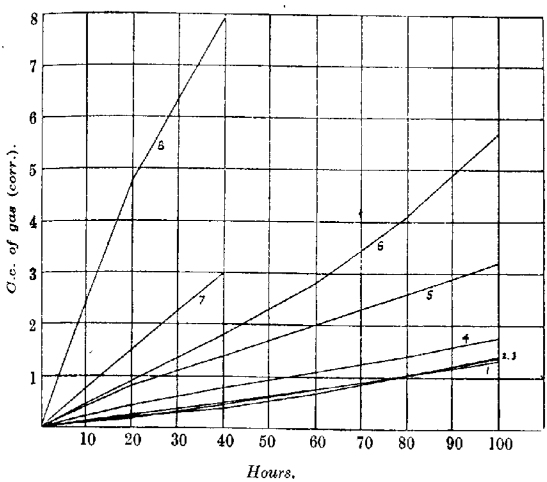
2 : 4 : 6-*Trinitrotoluene* (*various samples*) *at* 140°.

volume of gas from the individual tubes in the bath. If the deviation of temperature is within about 0·3°, it is generally sufficient to calculate a time correction for each day's readings, based on the mean temperature of the bath. Thus a deviation of 0·1° corresponds with a difference of 1·4 per cent. in the velocity, or 0·34 hour per day.

Measurements of Gas Evolution.

2:4:6-*Trinitrotoluene.*—Measurements at 120° gave very low results (about 0·15 c.c. in 100 hours). At 180° the evolution was too rapid and gave erratic accelerations, which made the measurements untrustworthy for comparison. Convenient velocities were obtained at 140°, and the following measurements were made on trinitrotoluenes from different sources (Fig. 4).

FIG. 5.



Trinitrotoluene isomerides at 140°.

Gas Evolution at 140° (*c.c. per gram*).

Melting point.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours
81·1°	0·35	0·69	1·04	1·31	1·56
81·05	0·39	0·78	1·16	1·47	1·75
81·05	0·12	0·33	0·70	0·94	1·13
81·0	0·14	0·28	0·54	0·85	1·13
81·0	0·16	0·32	0·55	0·85	1·13
81·0	0·16	0·35	0·58	0·78	0·99
81·0	0·12	0·22	0·37	0·57	0·77
80·95	0·25	0·50	0·86	1·21	1·50
80·95	0·14	0·28	0·52	0·83	1·10
80·75	0·33	0·68	0·86	1·01	1·26
80·65	0·26	0·54	0·85	1·13	1·36
80·65	0·33	0·71	0·90	1·07	1·24
78·80	0·36	0·71	1·09	1·45	1·80

Comparative measurements on dinitrotoluene gave no perceptible decomposition in 100 hours.

2:3:4-*Trinitrotoluene*.—The following figures show the gas evolution after one and two crystallisations respectively. The purification reduced the rate of decomposition slightly.

Gas Evolution at 140° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	
One crystallisation ...	0·44	0·78	1·07	1·40	1·75	Fig. 5 (4)
Two crystallisations ...	0·18	0·46	0·76	1·05	1·36	,, (3)
,, ,, ...	0·22	0·37	0·67	1·01	1·38	,, (2)
2:4:6-T.N.T. (mean)	0·24	0·49	0·77	1·04	1·29	,, (1)

3:4:6-*Trinitrotoluene*.—The commercial product was much less stable than the above, and decomposed so rapidly at 140° that the measurement had to be made at 120°. The results after one crystallisation are given at both temperatures.

Gas Evolution at 120° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
Original (sample *a*)	2·2	3·3	—	—	—
One crystallisation	0·55	1·08	1·58	2·05	2·48

Gas Evolution at 140° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	
Sample (*a*) One cryst.	4·7	7·9	—	—	—	Fig. 5 (8)
,, Two ,,	1·50	3·00	—	—	—	,, (7)
Sample (*b*) One cryst.	0·89	1·80	2·80	4·10	5·70	,, (6)
,, Two ,,	0·76	1·38	1·99	2·60	3·23	,, (5)

Even after purification, this isomeride was much less stable than 2:3:4-trinitrotoluene.

Mixtures of the Isomeric Trinitrotoluenes.—In order to ascertain whether the unsymmetrical isomerides, which always accompany 2:4:6-trinitrotoluene in small quantity in the crude product, affect the stability, the following mixtures were examined.

Gas Evolution at 140° (*c.c. per gram*).

2:3:4-T.N.T., per cent.	3:4:6-T.N.T., per cent.	Sample.	Purification.	2:4:6-T.N.T., per cent.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
—	—	—	—	100	0·16	0·34	0·57	0·78	0·99
1	—	*a*	coml.	99	1·03	1·55	2·12	2·60	3·01
1	—	*b*	coml.	99	0·23	0·80	1·40	2·01	2·53
1	—	*b*	2 crysts.	99	0·15	0·33	0·55	0·79	0·98
5	—	*a*	coml.	95	2·23	3·34	4·21	4·99	5·78
5	—	*a*	1 cryst.	95	0·31	0·77	0·98	1·23	1·52
5	—	*b*	1 cryst.	95	0·54	0·87	1·10	1·36	1·69
5	—	*b*	2 crysts.	95	0·17	0·44	0·52	0·78	0·98
—	1	*b*	1 cryst.	99	0·48	1·11	1·61	2·10	2·53
—	1	*a*	2 crysts.	99	0·10	0·67	1·02	1·37	1·62
—	1	*b*	2 crysts.	99	—	—	—	—	1·28
—	5	*a*	2 crysts.	95	2·01	2·85	3·45	4·02	4·60
—	5	*a*	2 crysts.	95	1·56	2·51	3·22	3·85	4·44
—	5	*b*	2 crysts.	95	—	—	—	—	2·71

Influence of Picric Acid on the Stability of 2:4:6-*Trinitrotoluene.*—A trinitrotoluene was tested alone and in admixture with picric acid. The evolution from the mixture was less than from trinitrotoluene alone.

Picric acid.	2:4:6-T.N.T.	C.c. of gas (corr.) (140°). 20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	150 hours.	200 hours.
2	—	0·14	0·25	0·29	0·35	0·44	0·62	0·83
2	2	0·14	0·22	0·25	0·32	0·42	0·62	0·81
2	2	0·15	0·23	0·28	0·34	0·43	0·68	0·95
—	2	0·25	0·50	0·74	0·96	1·19	1·94	2·88

Influence of Unsaturated Compounds.—To avoid a disturbing effect on the gas volume due to vapour pressure, castor oil was chosen, as a fairly non-volatile, unsaturated substance. This increased the rate of decomposition very strongly; even at 120°, the gas evolution from trinitrotoluene containing 5 per cent. of castor oil was readily measurable.

2:4:6-T.N.T.	Castor oil.	C.c. of gas (corr.) (120°). 20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	150 hours.	200 hours.
5	0·25	0·65	1·00	1·90	2·80	3·75	7·60	11·10

Naphthalene under similar conditions gave no measurable gas evolution in admixture with trinitrotoluene, even when present to the extent of 40 per cent.

Picric Acid.—Measurements were made at 140° and 183° on picric acid crystallised from water. The gas evolution was very rapid at the higher temperature, but showed some decrease in velocity as the decomposition proceeded, from which it would

appear that some catalyst was being gradually eliminated. The successive crystallisations did not reduce the rate of decomposition at 183°, but at 140° some stabilisation was noticeable in the latter crystallisations.

Gas Evolution at 140° (*c.c. per gram*).

	100 hours.	150 hours.	200 hours.	300 hours.
Original	0·11	0·27	0·44	0·88
Cryst. No. 2	0·13	0·35	0·51	0·92
„ „ 4..............	0·04	0·12	0·23	0·50
„ „ 5..............	0·06	0·21	0·31	0·58

Gas Evolution at 183° (*c.c. per gram*).

	1 hour.	2 hours.	3 hours.	5 hours.	10 hours.	15 hours.	20 hours.
Cryst. No. 1	2·90	4·50	5·45	6·45	—	—	—
„ „ 2	2·95	4·85	6·10	7·30	—	—	—
„ „ 3	2·30	3·95	5·20	6·15	8·35	10·60	12·80
„ „ 4	1·90	3·80	5·50	6·65	9·00	11·35	13·65
„ „ 5	2·05	3·90	5·65	6·95	9·20	11·50	13·80

As in the case of trinitrotoluene, castor oil increased the decomposition. Whereas picric acid alone gave practically no measurable decomposition at 120°, a mixture of picric acid with 5 per cent. of castor oil gave the following evolution:

Picric Acid, 5 *grams. Castor Oil,* 0·25 *gram.*

	50 hours.	100 hours.	150 hours.	200 hours.
C.c at 120°..............	0·85	2·50	4·70	6·85

1:3:5-*Trinitrobenzene.*—The gas evolution from this compound was very low, even at 183° (boiling aniline bath). The following rates of decomposition were obtained with different samples:

Gas Evolution at 183° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0·05	0·14	0·20	0·27	0·33
	0·04	0·09	0·13	0·18	0·23
	0·03	0·07	0·10	0·14	0·19
	—	0·10	0·13	0·15	0·18
	—	0·10	0·13	0·15	0·18
	—	0·15	0·19	0·25	0·30
Mean......	0·04	0·11	0·15	0·19	0·23

In order to ascertain the effect of storage on the stability, samples were kept for a year at 50°, and tested as above at 183°.

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0·07	0·13	0·18	0·24	0·30
	0·08	0·13	0·17	0·23	0·28
	0·06	0·10	0·17	0·22	0·27
	0·06	0·07	0·16	0·22	0·26
Mean......	0·07	0·11	0·17	0·23	0·28

The influence of hydrolysis was examined by keeping samples for a year in a saturated atmosphere at 45° and testing at 183°.

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0·04	0·08	0·13	0·17	0·17
	0·02	0·04	0·12	0·25	0·24
	0·01	0·02	0·10	0·11	0·15
Mean......	0·02	0·05	0·12	0·18	0·19

The effect of an admixture of picric acid on trinitrobenzene was tried at 150°, as the decomposition of picric acid itself is too rapid at 183°.

Gas Evolution at 150°.

	100 hours.	200 hours.	300 hours.	400 hours.	500 hours.
Picric acid, 0·2 gram; Trinitrobenzene, 1·8 grams ...	0·07	0·26	0·86	1·45	2·22
Trinitrobenzene 1·8 grams	0·07	0·07	0·20	0·28	0·60

Summary.

An apparatus is described for the determination of stability of high explosives by the velocity of evolution of gas on heating in a vacuum.

All explosives appear to be liable to a gradual decomposition at temperatures considerably below their ignition points. The velocity is highly affected by temperature and by the catalytic action of impurities.

Trinitrotoluene and the isomerides which accompany it on nitration of toluene do not differ greatly in stability when purified. Trinitrobenzene is much more stable, notwithstanding the difficulty with which it is prepared by nitration, and trinitrophenol shows an intermediate stability.

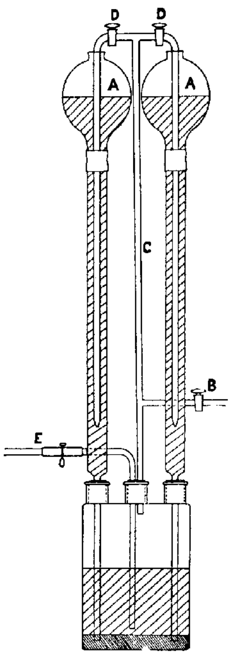
The thanks of the author are due to the Director of Artillery for permission to publish these results.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, November 3rd,* 1920.]

CLIX.—*The Preparation of Pure Carbon Dioxide.*

By Robert Crosbie Farmer.

The difficulty of preparing carbon dioxide completely free from air is frequently encountered. Notwithstanding that all solutions used for making the gas are previously boiled, the elimination of the last traces of air is very difficult, and the same applies to carbon dioxide from cylinders, even though most of the gas is blown to waste beforehand, to eliminate the air as far as possible. The difficulty is especially noticeable in the testing of the stability of gun-cotton by Will's method (*Zeitsch. angew. Chem.*, 1901, **14**, 743, 774), in which a relatively large quantity of carbon dioxide is used to sweep out the nitrogenous gases, and the air-correction forms a very high proportion of the unabsorbed gases.



By the following simple method, which has been used very satisfactorily for some time in connexion with the Will test, the proportion of air in carbon dioxide can be reduced to such a degree that it is practically immeasurable. The method depends upon the principle that a dissolved gas can be very completely removed from a liquid by bubbling a second gas through the liquid. The carbon dioxide is prepared from solutions of potassium hydrogen carbonate and sulphuric acid, each of which is freed from air by bubbling carbon dioxide through it, before the two are brought together.

The generator is shown in the figure. The pear-shaped funnels, *A A*, contain potassium hydrogen carbonate (300 grams to 1 litre of water) and sulphuric acid (120 c.c. to 1 litre of water) respectively. The solutions should be previously filtered through glass-wool. From the funnels these solutions pass down the broad verti-

cal tubes into the generating bottle. The bulk of the carbon dioxide is drawn off at *B* and used as required. A small proportion of the gas is, however, allowed to pass through the tube *C*, and bubbles through the columns of liquid in the two upright tubes, thus removing all traces of dissolved air. If desired, a separate source of carbon dioxide can be used for this purpose. As soon as the air originally present in the Woulfe's bottle has been eliminated, the carbon dioxide reaches a state of extreme purity, and gives practically no residue of gas on absorption with potassium hydroxide solution.

The fittings of the Woulfe's bottle must be absolutely free from leaks; the bottle may, if desired, be immersed in water covered with a layer of paraffin wax. The feed tubes dip below the surface of mercury to avoid back-diffusion. If the whole apparatus is mounted n a stand, it can be tilted slightly to equalise the back pressure in he two feed tubes, but no very accurate balancing is necessary. A ttle methyl-orange in the solution serves to show that the solutions re being mixed in about the right proportions.

Once started, the apparatus need never be disconnected. When he tap *B* is turned off, the introduction of the reagents automatically ceases. The taps *DD*, which regulate the bubbles of gas, should, owever, be closed when the apparatus is not in use. The spent quor can be drawn off at *E*, as the fresh solutions are added. The ate of evolution can be increased almost indefinitely by using a omewhat larger apparatus.

The thanks of the author are due to the Director of Artillery for ermission to publish this note.

RESEARCH DEPARTMENT,
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LX.—*Triphenylarsine and Diphenylarsenious Salts.*

By WILLIAM JACKSON POPE and EUSTACE EBENEZER TURNER.

HE introduction of aromatic arsenic compounds as materials for hemical warfare rendered necessary the working out of satisfactory methods for preparing triphenylarsine, $(C_6H_5)_3As$, and phenylchloroarsine, $(C_6H_5)_2AsCl$. The former of these two compounds is conveniently prepared by Michaelis and Reese's method Ber., 1882, **15**, 2876), which consists in treating an ethereal lution of arsenic trichloride and bromobenzene with sodium; in

a later paper (*Ber.*, 1886, **19**, 1031), Philips showed that chlorobenzene can be substituted for bromobenzene, and that the reaction is stimulated by the addition of a small proportion of ethyl acetate, but, more recently (*Annalen*, 1902, **321**, 160), Michaelis claimed that a cleaner product is obtained by the use of bromobenzene than of chlorobenzene.

The several workers on this reaction used ether as a solvent, and it was important to ascertain whether this could be replaced by some less volatile and less inflammable diluent. Preliminary experiments showed that the reaction proceeds better in benzene than in ethereal solution, and that, contrary to Michaelis's suggestion, chlorobenzene gives a cleaner product than does bromobenzene. It was thus shown that triphenylarsine is readily prepared by the action of sodium on a mixture of arsenic trichloride and chlorobenzene in benzene solution to which a little ethyl acetate had been added; this method was described in a report to the Chemical Warfare Department, dated January 28th, 1918, and formed the basis of the larger-scale work done by Morgan and others (this vol., p. 777) in the conversion of the laboratory method into a works process.

It was observed that the use of ether as a diluent is disadvantageous, in that the violent reaction tends to pass out of control, and that, when this happens, pyrophoric sodium remains after the evaporation of the ether, causing dangerous fires. The repetition of the method of Philips gave a yield of 71 per cent. of the theoretical; Michaelis's later method gave a yield of 67 per cent. of the theoretical. In the absence of a diluent, sodium acts on a mixture of arsenic trichloride and chlorobenzene causing incandescence.

Experiments were next carried out for the purpose of ascertaining how the yield of triphenylarsine is influenced by the proportions of the reacting materials and by the conditions. The general method adopted was to weigh out the sodium in slices (*s*), granules (*g*), powder (*p*), or wire into a large flask, cover with benzene containing 1 or 2 per cent. of ethyl acetate, allow to remain for half an hour to activate the metal, and then slowly run in the arsenic trichloride and chlorobenzene. After a few minutes a vigorous reaction sets in, which, when sodium wire is used, must be controlled by the use of a freezing mixture; when sliced sodium is used, no external cooling is necessary, and, indeed, once the reaction is checked by cooling, it can only be started again with considerable difficulty. The mixture is then left overnight, filtered, and the inorganic residue well washed with hot benzene; the filtrate and washing are distilled until a thermometer placed

n the liquid registers 200°. The residue solidifies on cooling to a rystalline mass, and is almost pure triphenylarsine; in general, it nelts at above 56°.

The following table gives the results of a series of experiments, n each of which 136 grams of chlorobenzene were used; this quantity requires theoretically 60 grams of arsenic trichloride and 16 grams of sodium for complete conversion into triphenylarsine.

No. of experiment.	Volume of benzene. C.c.	Sodium. Grams.	Form of sodium.	$AsCl_3$. Grams.	Percentage of theoretical yield of C_6H_5Cl used.
1	400	68	s	72	67·5
2	,,	,,	,,	,,	69
3	,,	,,	,,	,,	66
4	,,	,,	,,	,,	64
5	,,	,,	,,	,,	62·5
6	,,	,,	,,	,,	71
7	,,	,,	p	,,	83
8	,,	,,	s	80	91·5
9	,,	,,	,,	85	95·5
10	,,	,,	,,	90	93·5
11	,,	63	,,	80	80
12	,,	60	g	,,	75
13	350	,,	s	,,	83·5
14	,,	56	,,	90	81
15	300	60	,,	85	88
16	,,	57	,,	,,	93
17	,,	,,	,,	90	89
18	,,	,,	g	85	80
19	,,	55·5	s	90	83
20	,,	,,	,,	95	74·5
21	,,	,,	,,	90	84

Experiments 1 to 3 were carried out just as described above; 4 and 5 were carried out as rapidly as possible, and the product vas worked up immediately without remaining overnight. In numbers 6 and 7 the product was gently boiled under reflux for several hours after the spontaneous reaction had ended. It is thus shown that the yield is not improved by hastening the reaction, but that it does increase when the reaction is continued further by boiling; the operation of boiling under reflux was therefore introduced in all the later experiments. A consideration of the further experiments shows that the yield of triphenylarsine, calculated on the amount of chlorobenzene used, is appreciably raised by increasing the amount of arsenic trichloride to 85 grams, and is practically unaffected by diminishing the weight of sodium to 57 grams; it appears, further, that the volume of benzene used can be reduced to 300 c.c. without ill-effect on the yield. The most satisfactory results seem to be obtained by using 300 c.c. of benzene for each 136 grams of chlorobenzene, 85 grams of arsenic trichloride, and 57 grams of sodium, but since the

reaction proceeds well with considerable fluctuations of the pr portions, the appropriate quantities of materials to be used depen on the relative cost of the latter.

The reaction between chlorobenzene and arsenic trichloride not promoted by boiling with copper or aluminium powder, th copper-zinc couple, or magnesium or calcium turnings. The coppe arsenide obtained by digesting a hydrochloric acid solution arsenic trichloride, collecting the black powder, washing it wit water and acetone, and drying, is without action on chlorobenzene, but when heated with iodobenzene yields diphenyl.

Conversion of Triphenylarsine into Di- and Mono-phenylarsine Derivatives.

Michaelis and Reese showed (*Ber.*, 1882, **15**, 2876) that phenyl arsenious dichloride is produced on heating triphenylarsine with arsenic trichloride under pressure; it is to be concluded th diphenylarsenious chloride is formed as an intermediate stage, ar particulars have been given by Morgan and Vining (this vol p. 780) of a convenient means for preparing diphenylarsenio chloride by heating triphenylarsine with arsenic trichloride a 250—280° under pressure. This method involves, however, th use of an autoclave, and it seemed of interest to ascertain whethe the same reaction could be carried out under the ordinary atmo spheric pressure.

Triphenylarsine (30·6 grams) was maintained at 350° while arsenic trichloride (25·5 c.c.) was very slowly run in by means of a long capillary tube; the arsenic trichloride which distilled over was returned to the reaction vessel. The first addition of the arsenic trichloride occupied one and three-quarter hours. On carefully distilling the product under 12—15 mm. pressure, the following fractions were obtained at above 120°: (*a*) 120—160°, 17·7 grams; (*b*) 160—200°, 22·2 grams; (*c*) 200—250°, 2·2 grams; (*d*) residue, 2·2 grams. The fraction (*a*) is fairly pure pheny arsenious dichloride, (*b*) is pure diphenylarsenious chloride, while (*c*) and (*d*) consist of nearly pure triphenylarsine; allowing fo the recovery of the latter, the yield of phenylarsenious dichloride and diphenylarsenious chloride is 97 per cent. of the theoretical.

In the experiment just described, the arsenic trichloride was added fairly rapidly, and another may be quoted to show the effect of running it in more slowly. Using the same quantities as before, but taking seven hours for the addition of the arsenic trichloride, the following fractions were obtained on distilling the product under 12—15 mm. pressure: (*a*) 120—160°, 12 grams of

moderately pure phenylarsenious dichloride; (*b*) 160—205°, 31·5 grams of practically pure diphenylarsenious chloride; and a residue (*c*) of 7·2 grams of impure triphenylarsine. In this case, a larger proportion of diphenylarsenious chloride was produced.

The general conclusion is drawn from the above and other experiments that, under atmospheric pressure, the following reactions occur: $(C_6H_5)_3As + 2AsCl_3 = 3(C_6H_5)AsCl_2$ and

$$2(C_6H_5)_3As + AsCl_3 = 3(C_6H_5)_2AsCl.$$

In addition to the foregoing, the reaction represented by the following equation may also occur:

$$(C_6H_5)AsCl_2 + (C_6H_5)_3As = 2(C_6H_5)_2AsCl,$$

and experiment showed this reaction to take place almost quantitatively. On heating a mixture of triphenylarsine (15·3 grams) and phenylarsenious dichloride (11·2 grams) for four hours at 300° in an open flask, and distilling the resulting pasty mass under diminished pressure, nearly pure diphenylarsenious chloride (20 grams) distilled at 185°/15 mm.; this corresponds with a yield of about 80 per cent. of the theoretical; under the conditions stated, a small amount of chlorobenzene was produced, and practically no action occurs at 250°.

It is thus proved that the reaction between arsenic trichloride and triphenylarsine proceeds very satisfactorily under atmospheric pressure, and that the product is an equilibrium mixture resulting from the simultaneous occurrence of several reactions. In view of the possible importance of the observation that triphenylarsine can be converted into phenylarsenious dichloride and diphenylarsenious chloride by the action of arsenic trichloride under the ordinary pressure, the above and analogous reactions were protected by secret Patent No. 142880 of June 11th, 1918, of which the specification has now been published.

Diphenylarsenious Bromide, $(C_6H_5)_2AsBr$.

Diphenylarsenious oxide, $[(C_6H_5)_2As]_2O$, was prepared by Michaelis and La Coste (*Annalen*, 1880, **201**, 229), but the following is a more expeditious method for obtaining it in a pure state. Potassium hydroxide (12 grams) dissolved in water (10 c.c.) is added to rectified spirit (200 c.c.); a solution of diphenylarsenious chloride (53 grams) in spirit (100 c.c.) is added, and the mixture boiled for an hour. The solvents are then distilled off and the solid residue is extracted with chloroform; on drying, filtering, and evaporating the extract, a quantitative yield of pure diphenylarsenious oxide remains as a colourless, crystalline solid melting at 89—91°.

On heating the oxide at 100° with hydrobromic acid in a sealed tube and allowing to cool, diphenylarsenious bromide, $(C_6H_5)_2AsBr$, separates as a colourless, crystalline solid melting at 55—56°; this compound is described by Michaelis and La Coste as a yellow, oily liquid. The bromide is also obtained by heating triphenylarsine (30·6 grams) with arsenic tribromide (15·8 grams) for three hours at 300—350°; on distilling the product under 14 mm. pressure, the following fractions resulted: below 170°, 2 grams of a mixture of benzene and bromobenzene; 170—205°, 26 grams of crude diphenylarsenious bromide and a residue of 15 grams of mixed diphenylarsenious bromide and triphenylarsine. By redistillation, pure diphenylarsenious bromide was readily obtained.

Diphenylarsenious Iodide (Diphenyliodoarsine), $(C_6H_5)_2AsI$.

This previously undescribed substance is obtained by heating diphenylarsenious oxide (25 grams) with fuming hydriodic acid (30 grams) for two hours in a sealed tube at 100°; on cooling, the crude iodide (29·5 grams) solidifies and melts at 42—45°. On crystallisation from benzene, the compound is obtained in yellow, crystalline scales melting at 45—46° (Found: I=35·6. $C_{12}H_{10}IAs$ requires I=35·6 per cent.).

On heating triphenylarsine (30·6 grams) with arsenic tri-iodide (22·8 grams) for six hours in an open flask at 350—360° and distilling the resulting mass under diminished pressure, practically pure diphenylarsenious iodide (25 grams) distils at 204—218°/10 mm.; the yield is less than 50 per cent. of the theoretical, and the reaction does not proceed so satisfactorily as in the case of the corresponding bromo-derivative.

The work described in the present paper was carried out for the purposes of the Chemical Warfare Department, and permission for its publication has been given by the General Staff.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE.

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CLXI.—*Interaction of Ethylene and Selenium Monochloride.*

By Harold William Bausor, Charles Stanley Gibson, and William Jackson Pope.

In a previous paper (this vol., p. 271) we have shown that ethylene is absorbed by sulphur monochloride, giving a quantitative yield of $\beta\beta'$-dichloroethyl sulphide, in accordance with the following equation:

$$2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2S + S.$$

It is now shown that ethylene reacts with selenium monochloride to give *ββ'-dichloroethyl selenide dichloride* and selenium; the reaction proceeds in good accord with the following equation:

$$2CH_2{:}CH_2 + 2Se_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2SeCl_2 + 3Se.$$

Whilst it thus appears that sulphur monochloride and selenium monochloride are acted on quite differently by ethylene, it is possible that the action proceeds analogously in both cases so as to yield $\beta\beta'$-dichloroethyl sulphide or selenide, but that the selenide is further acted on by selenium monochloride, giving selenium and the new derivative of quadrivalent selenium now described; this suggestion is supported by the observations of Evans and Ramsay (T., 1884, **45**, 64), which indicate that selenium monochloride readily decomposes into selenium and chlorine.

Preparation of Selenium Monochloride.

Selenium monochloride is conveniently prepared in quantity by modification of the method described by Divers and Shimose (T., 1884, **45**, 198). Finely powdered selenium (80 grams) is added, with constant shaking, to fuming sulphuric acid (320 c.c.) containing 15 per cent. of dissolved sulphur trioxide; the mixture is warmed to 45—50°, with shaking, allowed to cool, and treated with a current of dry hydrogen chloride. When the gas is no longer absorbed, the product is poured into concentrated sulphuric acid (450 c.c.), and the residue washed in with the same liquid (5 c.c.); the lower layer of crude selenium monochloride containing suspended selenium, is drawn off, mixed with fuming sulphuric acid (containing 15 per cent. of sulphur trioxide) (100 c.c.), and treated with a brisk stream of dry hydrogen chloride for an hour and a-half. The product is now poured into concentrated sulphuric acid (150 c.c.), when much hydrogen chloride is evolved,

and the lower layer of selenium monochloride (99 grams) drawn off. Thus obtained, it forms a deep red liquid containing a little free selenium in suspension; it is further purified by keeping over dry potassium chloride and filtering in a dry atmosphere.

ββ′-Dichloroethyl Selenide Dichloride, $(CH_2Cl\cdot CH_2)_2SeCl_2$.

Selenium monochloride (55·5 grams) is dissolved in dry benzene (50 c.c.), and a current of dry ethylene passed through the solution; considerable evolution of heat occurs, and the liquid should be kept cool. Absorption commences rapidly, and selenium is almost immediately precipitated; it is desirable to add further quantities of dry benzene (20 c.c.) to prevent blockage of the delivery tube. When no further absorption occurs, more benzene is added, and the liquid filtered boiling hot, the residue being extracted with boiling benzene until the filtrate deposits no more crystalline product on evaporation. ββ′-Dichloroethyl selenide dichloride (27·5 grams) remains in the form of white, crystalline needles after distilling off the benzene, and may be purified from slight admixture with selenium by recrystallisation from boiling benzene. From observation of the quantity of selenium recovered (30·0 grams), it is concluded that the reaction proceeds in accordance with the equation given above.

ββ′-Dichloroethyl selenide dichloride is about ten times as soluble in boiling benzene as in the cold solvent; it crystallises in long, colourless prisms (see figure), which melt at 122·5°, and are slightly hygroscopic. The crystallographic description given below was furnished by Miss I. E. Knaggs, working under the direction of Mr. A. Hutchinson.

Crystal System.—Monosymmetric, holohedral.

Axial Ratios.—$a:b:c = 0{\cdot}6345 : 1 : 0{\cdot}8389$. $\beta = 75°50'$.

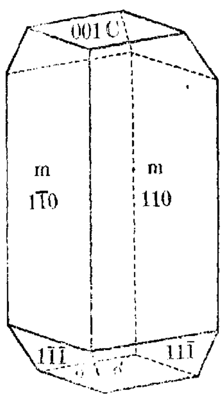
Forms Observed.—$C(001)$, $m(110)$, $o'(111)$.

Angle.	No. of measurements.	Limits.	Observed.	Calculated
$mm = 1\bar{1}0 : 110$	9	62°38′— 63°46′	63°12′	—
$mm = 110 : \bar{1}10$	9	116 14 —117 22	116 52	116°48′
$mo' = \bar{1}10 : \bar{1}11$	9	35 25 — 36 24	36 2·5	—
$o'C = \bar{1}11 : 001$	7	65 24 — 66 43	66 2	65 59·5
$mC = \bar{1}10 : 001$	6	101 40 —102 23	102 2	—
$Cm = 001 : \bar{1}10$	7	77 25 — 78 28	77 49	77 58

No cleavage was observed. The crystal habit is prismatic, an is terminated by small basal and pyramidal planes. The cryst faces are very much rounded and badly developed, and it was onl possible to obtain approximate angular measurements. The opt

xial plane is perpendicular to the plane of symmetry, and the cute bisectrix lies in the plane of symmetry, being inclined at 2° to the z-axis in the acute axial angle. The refractive index, β, as found by the immersion method to be approximately 1·65; he index, α, is slightly less than this, and γ is somewhat higher han 1·75, and could not be determined. The double refraction s hence strong and positive in sign; this was verified by observa-tion on a section cut nearly perpendicular to the acute bisectrix. The optical axial angle was measured as 31°13′ for sodium light in a liquid of refractive index 1·65. Moderate dispersion of the optic axes was observed, the angle for red being greater than that for blue light; horizontal dispersion was not observed.

The compound dissolves freely in cold water to an acid liquid,



hich gives a precipitate of silver chloride with the nitrate; a iscous liquid remains on evaporating the aqueous solution. One alf of the chlorine present is hydrolysed to hydrogen chloride by he action of water (Found: C=17·5; H=2·70; Cl=51·4; Se=29·1. 0·1591 required 11·5 c.c. N/10-$AgNO_3$. Hydrolysable chlorine=25·7. $C_4H_8Cl_4Se$ requires C=17·3; H=2·89; Cl=51·3 per cent.).

On passing sulphur dioxide into a cold dilute aqueous solution of the dichloride, a heavy oil separates; this, when collected and left in a cool place, crystallises to a mass of almost colourless, prismatic needles. This compound is very readily soluble in benzene, and, when crystallised from a small quantity of this solvent, melts at 23—25°; it is possibly $\beta\beta'$-dichloroethyl selenide,

and, as special precautions must be observed in handling such a substance, its further examination will be continued later. We are engaged on the further study of the interaction of ethylene and other non-metallic chlorides.

The work described in the present paper was carried out for the purposes of the Chemical Warfare Department, and permission for its publication has been given by the General Staff.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, October 15th*, 1920.]

CLXII.—*Researches on Residual Affinity and Co-ordination. Part II. Acetylacetones of Selenium and Tellurium.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

THE acetylacetone derivatives of the metals, metalloids, and non-metals may be classified into three main groups.

I. Metallic acetylacetones, in which the principal valencies of the metal are completely satisfied by the univalent acetylacetone radicle, $C_5H_7O_2$, such as the thallous, glucinum, cupric, zinc, scandium, aluminium, chromic, ferric, and thorium derivatives, and numerous others. In many instances acetylacetone has given wings to the metals, for certain of these compounds are volatile without decomposition (Combes, *Compt. rend.*, 1894, **117**, 1222; Kurovski, *Ber.*, 1910, **63**, 1078; T., 1913, **103**, 81; 1914, **105**, 189).

II. Acetylacetones of the non-metals and metalloids, in which the principal valencies of the element are only partly satisfied by the univalent acetylacetone radicle. Such are the compounds of boron, silicon, and titanium, $B(C_5H_7O_2)_2Cl$, $Si(C_5H_7O_2)_3Cl$, and $Ti(C_5H_7O_2)_3Cl$, which function as metallic chlorides giving rise to remarkable double salt (Dilthey, *Annalen*, 1905, **344**, 326).

III. Acetylacetones of sulphur, which behave as true organic derivatives of sulphur, carbon being attached directly to this non-metal and not through the intermediary of oxygen, as in the two preceding classes (Angeli and Magnani, *Gazzetta*, 1893, **23**, ii, 415; 1894, **24**, i, 342; Vaillant, *Compt. rend.*, 1894, **119**, 647).

There is also a transition group of metallic acetylacetones between the main groups I and II, in which the principal valencies of the metal are only partly satisfied by the acetylacetone complex. This

transition group includes the complex acetylacetones of platinum (Werner, *Ber.*, 1901, **34**, 2584) and the cobaltic acetylacetone compounds of the general type $[C_5H_7O_2Co\ en_2]X_2$ (Werner, *Helv. Chim. Acta*, 1918, **1**, 78), where en = ethylenediamine. The latter series of acetylacetone derivatives exhibits optical activity and the existence of enantiomorphous pairs of isomerides affords definite information as to the arrangement of the acetylacetone nucleus in these substances, and justifies the belief that the univalent group $CH_3{\cdot}CO{\cdot}CH{:}C(CH_3){\cdot}O{\cdot}$ functions as two associating units,* forming a ring structure in which the metallic atom is implicated.

The research described below, which is still in a preliminary stage, shows that the interactions of acetylacetone and the tetrachlorides of selenium and tellurium lead to products differing considerably in type from those classified above. Although there are many points of difference between the various members of the three main groups of acetylacetone derivatives, they possess one attribute in common, namely, the univalent acetylacetone radicle, of which one or more are present in the molecule of every one of these derivatives hitherto described. In the acetylacetones of selenium and tellurium these metalloids are found to be associated with a bivalent radicle, $C_5H_6O_2''$.

Selenium tetrachloride and acetylacetone interact in ethereal solution in accordance with the following equation:

$$(1)\ 2SeCl_4 + 4C_5H_8O_2 = [C_5H_6O_2{:}Se]_2 + 2C_5H_7ClO_2 + 6HCl,$$

the products being *selenium acetylacetone*, a well-defined, pale yellow, crystalline compound, chloroacetylacetone, and hydrogen chloride. This selenium acetylacetone, which is bimolecular in benzene solution, is readily decomposed by concentrated hydrochloric acid and by reducing agents, such as the alkali hydrogen sulphites. The former of these decompositions takes place readily, giving rise to elemental selenium and chloroacetylacetone,

$$(2)\ [C_5H_6O_2{:}Se]_2 + 2HCl = 2Se + 2C_5H_7O_2Cl.$$

* The adjective "chelate," derived from the great claw or "chela" ("chely") of the lobster and other crustaceans, is suggested for these caliper-like groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings. Among the compounds which, by virtue of their residual affinity, function as chelate groups are ethylenediamine (en), propylenediamine, αα-dipyridyl and dimethylethylene sulphide (T., 1912, **101**, 1798). Many unsaturated radicles also function as chelate groups, partly owing to their principal valencies and partly owing to residual affinity, for example, the acetylacetone and oxalate groups, and the univalent groups in dimethylglyoxime,

$$CH_3{\cdot}C({:}NOH){\cdot}C(CH_3){:}NO{\cdot},$$

nitroso-β-naphthol, $O{:}C_{10}H_6{:}NO{\cdot}$, and many other lake-forming complexes. In the present communication the bivalent radicle, $C_5H_6O_2''$, functions as a chelate group entirely owing to its principal valencies.

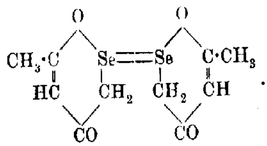
The latter decomposition, which proceeds quantitatively, is an interesting example of the way in which organic research sometimes leads to improvements in inorganic syntheses. Four molecular proportions of alkali hydrogen sulphite reduce the dimeric selenium acetylacetone quantitatively into acetylacetone and alkali selenodithionate:

$$(3)\ [C_5H_6O_2{:}Se]_2 + 4KHSO_3 = 2C_5H_8O_2 + 2Se{<}{}^{SO_3K}_{SO_3K}.$$

In the earlier preparations these selenodithionates were obtained in a laborious manner, together with alkali thioselenates, by digesting sulphites with selenium or selenious acid (Rathke, *J. pr. Chem.*, 1865, **95**, 8; 1866, **97**, 56; Schultze, *ibid.*, 1885, [ii], **32**, 399).

The acetylacetone set free in the foregoing reduction and in other similar reactions is conveniently estimated by coupling with sodium *iso-p*-nitrobenzenediazo-oxide to form the sparingly soluble *p*-nitrobenzeneazoacetylacetone, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_5H_7O_2$ (Bülow and Schlotterbeck, *Ber.*, 1902, **35**, 2191).

The foregoing equations representing the formation and quantitative decompositions of selenium acetylacetone are consistent with the view that this associated compound may be represented by the graphic formula



(I.)

This conclusion is confirmed by the results obtained in studying the interaction of tellurium tetrachloride and acetylacetone. In moderately concentrated chloroform solution these reagents give rise to a colourless substance, *tellurium acetylacetone dichloride*,

$$(4)\ TeCl_4 + C_5H_8O_2 = C_5H_6O_2{:}TeCl_2 + 2HCl.$$

The dichloride when cautiously reduced with sulphurous acid or alkali hydrogen sulphites loses its chlorine and yields *tellurium acetylacetone*, a golden-yellow compound, which, unlike its selenium analogue, does not exhibit association in organic solvents:

$$(5)\ C_5H_6O_2{:}TeCl_2 + H_2SO_3 + H_2O = C_5H_6O_2{:}Te + 2HCl + H_2SO_4.$$

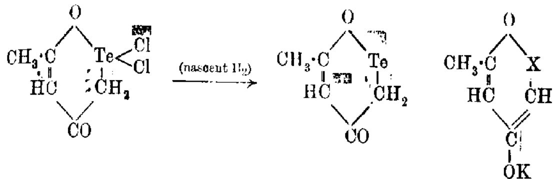
Tellurium acetylacetone is decomposed quantitatively into tellurium and acetylacetone by such reducing agents as an aluminium-mercury couple or alkali hydrogen sulphites. In the latter case a tellurium analogue of the alkali selenodithionates was not detected:

$$(6)\ C_5H_6O_2{:}Te + 2KHSO_3 = C_5H_8O_2 + Te + K_2SO_4 + SO_2.$$

Tellurium acetylacetone differs from the selenium analogue in its decomposition with cold concentrated hydrochloric acid (compare equation 2); it yields acetylacetone and half the tellurium as the tetrachloride:

$$(7)\ 2C_5H_6O_2{:}Te + 4HCl = 2C_5H_8O_2 + Te + TeCl_4.$$

These reactions support the view that tellurium acetylacetone dichloride (II) and tellurium acetylacetone (III) may be represented respectively by the following formulæ:



(II.) (III.) (IV.)

Selenium and tellurium acetylacetones function as weak acids and dissolve in aqueous alkali hydroxides. It is therefore evident that they may have an alternative enolic configuration (IV), which would correspond with that of their unstable alkali salts.

EXPERIMENTAL.*

Selenium Acetylacetone, $[C_5H_6O_2{:}Se]_2$.

Selenium tetrachloride was prepared by passing dry chlorine in excess over coarsely powdered selenium at the ordinary temperature, the dark red monochloride being formed as an intermediate phase. The pale yellow, crystalline tetrachloride (14·3 grams) suspended in 140 c.c. of dry ether was treated at the ordinary temperature with 13 grams of acetylacetone (2 mols.) dissolved in 30 c.c. of the same solvent. Hydrogen chloride was forthwith evolved, the solution reddened, the tetrachloride slowly passed into solution, while a yellow precipitate appeared and redissolved in about thirty minutes to a transparent, pale red, fuming lachrymatory solution, which was evaporated rapidly at the ordinary temperature in a current of air. Hydrogen chloride, ether, and chloroacetylacetone were thus removed; the residue, a pale red oil, solidified on stirring. The product (10 grams, yield 90 per cent.) crystallised from benzene in pale primrose-yellow, glistening plates or lath-like needles, giving yellow solutions in organic media; on exposure to light for prolonged periods its surface became thinly coated with pink selenium.

* The authors are indebted to Dr. Scott for a gift of pure tellurium, and to Professor Ling for specimens of this metalloid and of selenium.

During this incipient decomposition the odour which at first was pleasing and farinaceous became faintly nauseating, a result which was due probably to liberation of traces of hydrogen selenide. The substance reddened at about 140°, and subsequently melted and decomposed at 175°. In a sealed capillary tube heated from 150° it melted to an orange-red liquid at 185°.

The selenium was determined by heating the weighed substance with 5 c.c. of fuming nitric acid in a flask with ground-in air condenser. Oxidation being completed, the solution was boiled with excess of hydrochloric acid until all nitrous compounds were destroyed, the metalloid, precipitated as the red modification, transforming into the dark grey variety on warming with sodium sulphite or aqueous sulphurous acid, was collected and weighed. Carbon and hydrogen estimations were made in combustion tubes charged with fine copper oxide, a long length of lead chromate, and a spiral of copper oxide, a little of this oxide being also placed in the porcelain boat. In the combustion of selenium and tellurium derivatives more accurate results were obtained by burning with oxygen alone than with air followed by oxygen (Found, C=34·23, 33·74; H=3·45, 3·72; Se=44·10, 44·17. $(C_5H_6O_2Se)_n$ requires C=33·86; H=3·41; Se=44·68 per cent.).

Molecular determinations by the ebullioscopic method in benzene gave 316, 312 (0·65 and 1·18 grams per 100 c.c. respectively), thus indicating association: $n=1$ or 2 requires 177 or 354.

Selenium acetylacetone is not obtained unless the prescribed experimental conditions are followed closely in regard to temperature, concentration, proportion of reagents, and removal of the volatile products at the ordinary temperature. The proportion of two molecules of acetylacetone to one of selenium tetrachloride has been found to give the optimum yield, whereas ratios of one or four molecules of the diketone do not give rise to any crystalline product. Experiments carried out in chloroform or with selenium dibromide, Se_2Br_2, and acetylacetone in ether have led so far to elimination of selenium and to the production of lachrymatory oils. A preliminary experiment with benzoylacetone and selenium tetrachloride in cold ether indicated the formation of a pale yellow selenium benzoylacetone (m. p. 212°) having similar properties to selenium acetylacetone.

Selenium acetylacetone, which has a faintly acidic, sweetish taste, dissolves slightly in hot water, the solution being distinctly acid; it is somewhat sparingly soluble in boiling ether, ethyl alcohol, acetone or chloroform, and dissolves more freely in hot glacial acetic acid. Its solubility in boiling benzene is about 1·5 grams in 100 c.c., but is ten times less in the cold.

Selenium acetylacetone dissolves readily in cold aqueous alkali hydroxides or ammonia to bright yellow solutions, which regenerate the compound if neutralised at once with dilute acid. The alkaline solutions speedily decompose, red selenium being precipitated, whilst a nauseating odour is developed. Although insoluble in aqueous sodium carbonate, prolonged treatment with this reagent leads to the foregoing decomposition. The organic product of these alkaline decompositions is an oil having a pleasant ketonic odour.

Dilute mineral acids are without effect on selenium acetylacetone, concentrated nitric and sulphuric acids have a destructive action, whereas cold concentrated hydrochloric acid decomposes it smoothly into red selenium and chloroacetylacetone, identified by its boiling point, lachrymatory properties, and green copper derivative.

Ferric chloride either in aqueous or alcoholic solution gives no red coloration with selenium acetylacetone even after two hours. In twenty-four hours an orange tint is discernible, and this coloration is developed more quickly on boiling, but selenium is set free simultaneously. When distilled with zinc dust, selenium acetylacetone loses selenium, evolves a nauseating vapour, and gives rise to an oil which, after rectification, gives a red coloration with ferric chloride and has a pleasant ketonic odour. Iodine in chloroform solution has no action on selenium acetylacetone, but chlorine in the same solvent gives selenium tetrachloride and chloroacetylacetone, whereas bromine yields lachrymatory products and a colourless, crystalline substance (m. p. 180°). Aqueous hydrogen sulphide decomposes it slowly in the cold with liberation of sulphur and selenium. Hydroxylamine, phenylhydrazine, p-bromophenylhydrazine, p-nitrophenylhydrazine, and 6-chloro-3:4-tolylenediamine induce a more or less rapid elimination of selenium.

By-products of the Formation of Selenium Acetylacetone.—The amount of hydrogen chloride set free in the condensation was estimated and found to be equivalent to three-fourths of the chlorine originally present in the selenium tetrachloride. The chloroacetylacetone (b. p. 148—150°), of which more than two-thirds of the calculated amount were obtained in a purified condition, was further identified by conversion into its green copper derivative soluble in chloroform. These results support the view expressed by equation 2 (p. 1457).

Quantitative Decomposition of Selenium Acetylacetone: Alkali Selenodithionates.

Two grams of powdered selenium acetylacetone were added to 18 c.c. of water containing 3 grams of potassium metabisulphite ($2\frac{1}{2}$ mols. of $KHSO_3$ equivalent to 1 atom of Se), and the mixture

was shaken mechanically for one hour. A colourless, crystalline precipitate of potassium selenodithionate, $K_2S_2SeO_6$, was then collected, the filtrate extracted with ether to remove acetylacetone, and the aqueous layer mixed with alcohol to complete the deposition of the inorganic product (yield 3·5 grams = 97 per cent. of the theoretical). When separating rapidly from aqueous solution the selenodithionate appeared in lustrous scales or thin plates; when crystallising slowly it was obtained in long, transparent, silky needles.

Both forms of the salt were quite colourless and stable when exposed to air and light. On heating they commenced to redden at 190°, and at 250° the red selenium turned grey. Meanwhile sulphur dioxide was evolved, and finally a residue of potassium sulphate was left (Found, K = 24·59; S = 20·06, 20·58; Se = 25·06, 25·07. Calc., K = 24·63; S = 20·19; Se = 24·95 per cent.).

Sodium selenodithionate, $Na_2S_2SeO_6$, was produced by adding selenium acetylacetone to a cold concentrated solution of sodium hydrogen sulphite ($2\frac{1}{3}$ mols.), the mixture being shaken until the organic compound had dissolved, and precipitated, by adding alcohol, in colourless, lustrous anhydrous scales, readily soluble in water (Found, Na = 16·24. $Na_2S_2SeO_6$ requires Na = 16·12 per cent.). Aqueous sulphur dioxide had a similar action on selenium acetylacetone, dissolving it in the cold to a colourless solution containing acetylacetone, extracted by ether, and selenodithionic acid, which slowly decomposed into selenium, sulphur dioxide, and sulphuric acid.

Estimation of Acetylacetone.—The acetylacetone set free in the foregoing decompositions was identified by conversion into its pale blue copper and colourless aluminium derivatives. It was estimated by coupling with sodium *iso*-*p*-nitrobenzenediazo-oxide.

Selenium acetylacetone (0·2 gram) was shaken for four hours with 0·25 gram of potassium metabisulphite and 3 c.c. of water. Potassium selenodithionate was precipitated by alcohol, and the filtrate treated with 0·23 gram of sodium *iso*-*p*-nitrobenzenediazo-oxide, $(NO_2 \cdot C_6H_4 \cdot N_2 \cdot ONa, H_2O)$. The pale orange-red precipitate of *p*-nitrobenzeneazoacetylacetone, after washing with dilute alcohol, weighed 0·2 gram (calc., 0·28 gram), and gave the correct melting point, 219—222°.

Tellurium acetylacetone dichloride, $C_5H_6O_2{:}TeCl_2$.

Tellurium reacted with dry chlorine, evolving heat and forming tellurium tetrachloride as a yellowish-white liquid, in which excess of the metalloid dissolved to an almost black solution, probably containing the dichloride. With excess of chlorine the whole solidi-

fied to a yellow, crystalline mass of tetrachloride, which was purified by sublimation.

Sublimed tellurium tetrachloride (10·3 grams) was mixed with 7·6 grams of acetylacetone (2 mols.) in 55 c.c. of dry chloroform and the orange solution heated under reflux on the water-bath. The evolution of hydrogen chloride ceased after two hours' boiling; the solution was filtered from a heavy, dark grey oil, and concentrated over lime in a desiccator. Crystals of tellurium acetylacetone dichloride separated; the concentrated filtrates yielded further crops (yield 7 grams, or 62 per cent. calculated on $TeCl_4$). The product was sparingly soluble in ether, benzene, or chloroform, rather more so in hot alcohol, and very readily soluble in cold acetone. It crystallised from alcohol or benzene in acicular forms, and separated slowly from acetone in large, transparent, hexagonal prisms often twinned. Both forms were colourless; they darkened at 155—160° and melted and decomposed between 169° and 173°, liberating tellurium and evolving hydrogen chloride and a lachrymatory oil, which developed a red coloration with aqueous ferric chloride. The tellurium was estimated by warming a weighed amount with fuming nitric acid (5 c.c.) in a reflux apparatus. After boiling with concentrated hydrochloric acid (25 c.c.) to remove nitrous compounds, the solution was evaporated to dryness. The residue dissolved in 15 c.c. of 10 per cent. hydrochloric acid was warmed with 10 c.c. of 15 per cent. hydrazine hydrochloride and 35 c.c. of saturated sulphurous acid gradually added, the liberated tellurium being dried at 107°. The chlorine was estimated by alkaline hydrolysis and precipitation as silver chloride; the combustions were carried out as in the case of selenium acetylacetone (Found, C=20·72; H=2·07; Cl=24·01, 23·95; Te=42·87. $(C_5H_6O_2Cl_2Te)_n$ requires C=20·24; H=2·04; Cl=23·92; Te=43·00 per cent.).

Molecular-weight determinations by the ebullioscopic method in acetone (1·846 and 4·207 grams per 100 c.c.) gave 241 and 255 (M=296·5).

Tellurium acetylacetone dichloride does not become discoloured on exposure to light. It readily loses chlorine with hot water or aqueous acids or alkalis. Tellurium is not set free by boiling with aqueous potassium hydroxide. With aqueous ferric chloride a red coloration is developed only very slowly. When warmed with considerable excess of aqueous sulphurous acid this compound is decomposed completely, yielding tellurium and acetylacetone.

Tellurium Acetylacetone, $C_5H_6O_2{:}Te$.

The foregoing dichloride (2·2 grams) when triturated for ten minutes with 1·8 grams of potassium metabisulphite (1 mol.) and 20 c.c. of water yielded a small amount of tellurium and 1 gram (yield 60—70 per cent.) of a yellow compound, which was purified by crystallisation from benzene or hot water. This product was also obtained with less liberation of tellurium by boiling the dichloride with a slight excess of aqueous sulphur dioxide (Found, C=27·14, 26·62; H=2·88, 2·92; Te=56·55. $(C_5H_6O_2Te)_n$ requires C=26·61; H=2·68; Te=56·52 per cent.).

Molecular-weight determinations in boiling benzene and acetone (0·462 and 0·879 gram per 100 c.c.) gave respectively 262 and 185. M.W. for $n=1$ is 225·6.

Tellurium acetylacetone forms heavy, golden-yellow needles sparingly soluble in water, ether, chloroform, or alcohol, and decomposing indefinitely at 145—180°. In a sealed tube it melts to a yellow liquid, which partly sublimes in yellow needles, and on further heating decomposes with elimination of tellurium and production of an oil resembling acetylacetone. Under reduced pressure the compound sublimes at about 160° in glistening, yellow needles.

Tellurium acetylacetone resembles the selenium compound in its chemical reactions. It dissolves in cold aqueous potassium hydroxide to a bright yellow solution, from which immediate neutralisation with acid regenerates the original compound, but after a few minutes the alkaline solution deposits tellurium. Cold concentrated hydrochloric acid decomposes the compound with elimination of tellurium. Ferric chloride develops a red coloration, but only after a long time. Hydrogen peroxide decolorises immediately the yellow aqueous solution of tellurium acetylacetone, giving a white precipitate; hydrogen sulphide produces at once a black deposit (TeS_2 ?), alcoholic mercuric iodide yields a yellow precipitate, and warm aqueous sulphur dioxide reduces the compound with elimination of tellurium.

Quantitative Decompositions of Tellurium Acetylacetone.

(a) *With Bisulphite.*—Tellurium acetylacetone (0·4 gram) shaken for five hours with 0·4 gram of potassium metabisulphite and 3 c.c. of water yielded sulphur dioxide, 0·2 gram of tellurium, and 0·3 gram of potassium sulphate, the latter precipitated by alcohol after extracting the acetylacetone with ether.

Warm aqueous sulphur dioxide brought about a similar reduction, yielding acetylacetone, tellurium, and sulphuric acid.

(b) *With an Aluminium–Mercury Couple.*—Tellurium acetylacetone (0·4 gram) in 50 c.c. of hot water was shaken with an aluminium–mercury couple, and the solution, filtered from precipitated tellurium, was treated with sodium *iso-p*-nitrobenzenediazooxide (0·37 gram) in 8 c.c. of glacial acetic acid and 20 c.c. of absolute alcohol. After three hours the orange-red *p*-nitrobenzeneazoacetylacetone was collected (0·35 gram, yield 80 per cent.) and crystallised from glacial acetic acid; it then melted at 220°.

(c) *With Concentrated Hydrochloric Acid.*—A preliminary experiment showed that tellurium acetylacetone, unlike its selenium analogue, yielded acetylacetone and not chloroacetylacetone on decomposition with concentrated hydrochloric acid, a portion only of the tellurium being precipitated, whilst the remainder was left in solution as tellurium tetrachloride. Tellurium acetylacetone (0·1558 gram) was stirred with cold concentrated hydrochloric acid for several hours. The precipitated tellurium, which was then collected and washed successively with a little more concentrated acid and water, weighed 0·0432 gram. The filtrates were then treated with aqueous hydrazine hydrochloride saturated with sulphur dioxide. These reducing agents precipitated the remainder of the tellurium, which weighed 0·0427 gram (total amount of tellurium found = 0·0859 gram.; calc., 0·0880). These results confirm equation 7 (p. 1459).

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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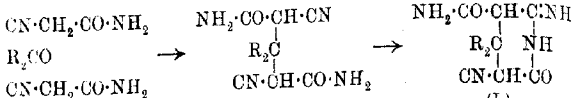
CLXIII.—*The Formation and Reactions of Imino-compounds. Part XX. The Condensation of Aldehydes with Cyanoacetamide.*

By JAMES NELSON EDMUND DAY and JOCELYN FIELD THORPE.

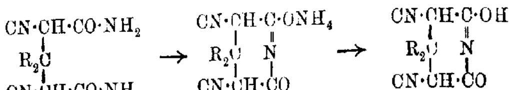
IN a series of papers dealing with the condensation of ketones with cyanoacetamide (T., 1911, **99**, 422; 1913, **103**, 1586; 1919, **115**, 686) it has been shown that the reaction between these substances in the presence of a condensing agent leads to the formation of *cis*-

and *trans*-additive products, and that ring-formation then ensues, yielding two different types of heterocyclic six-membered systems. Thus the *trans*-condensation proceeds:



(*trans.*) (I.)

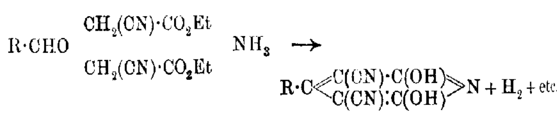
whereas the *cis*-condensation yields:



(*cis.*) (II.)

the compounds formed in this case (II) being the same as those produced by the well-known reaction discovered by Guareschi, which involves the interaction of ethyl cyanoacetate, the ketone, and ammonia. As both types (I) and (II) yield the $\beta\beta$-disubstituted glutaric acid on complete hydrolysis, the method serves as a useful one for the preparation of these important acids in quantity.

In the course of the work which is now being carried out at this College in connexion with the formation and properties of carbon ring structures it became evident that considerable quantities of the glutaric acids having a single substituent group in the β-position would be required, and search was therefore made for a similar general method which could be used for their production. Obviously the use of an aldehyde in place of a ketone in the above reaction suggested itself, but, unfortunately, Guareschi has already shown that, by his method, aldehydes lead to the formation of stable pyridine derivatives which cannot be hydrolysed to the nitrogen-free acid:



(III.)

It was therefore gratifying to find that the condensations between aliphatic aldehydes and cyanoacetamide proceeded very smoothly in the presence of a trace of alkali hydroxide, that yields of 90 per cent. or more were obtained, and that the condensation products could be quickly and completely hydrolysed to the corresponding β-substituted glutaric acid by means of dilute hydrochloric acid.

Moreover, the acids obtained were in a high state of purity and did not require further treatment before use. Evidently, therefore, the method is the best one at present known for the preparation of these acids.

Investigation quickly showed, however, that the condensation products formed in this way were of a different type from those produced in the ketone reactions. They were, for example, insoluble in dilute mineral acids, and were without basic properties. They did not form platinichlorides, and were not hydrolysed to the imide by boiling with mineral acids, a reaction characteristic of the ring imino-compounds of type I. They were, moreover, very much more readily hydrolysed to the nitrogen-free acid than the compounds of either type I or II, and were, in fact, undoubtedly open-chain cyanoamides formed in accordance with the scheme:

$$R\cdot CHO \quad \begin{array}{l} CH_2(CN)\cdot CO\cdot NH_2 \\ CH_2(CN)\cdot CO\cdot NH_2 \end{array} \quad \longrightarrow \quad R\cdot\begin{array}{l} CH(CN)\cdot CO\cdot NH_2 \\ | \\ CH \\ | \\ CH(CN)\cdot CO\cdot NH_2 \end{array}$$

(IV.)

This type of condensation product formed, in every case investigated, approximately 99 per cent. of the total solid obtained. The remainder comprised about equal quantities of the imino-imide of type I and the Guareschi compound of type III.

A consideration of these data seems to lead to the conclusion that there is a greater tendency to form six-membered heterocyclic structures when two alkyl groups are attached to the central carbon atom than when only one substituting group is in this position. If this were true and could be applied to homocyclic carbon systems of similar type, it would account for many of the peculiar properties which are possessed by compounds having two alkyl groups attached to the same carbon atom. On the other hand, it is possible that the physical properties of the condensation products may determine the order and amount of their formation. In other words, that whilst the normal compound of type IV is in every case the one first produced, its actual separation as the final product may be influenced by its solubility in the solvent used. Ring-formation may therefore ensue if the solubility of the initial compound prevents it from being removed by precipitation, and if the ring-compound happens to be the less soluble of the two. In support of this view it is to be noted, as already mentioned, that there is definite evidence of ring-formation of both types I and II in the aldehyde condensations. Against it must be placed the fact that, although repeated attempts have been made by varying the solvent,

no variation in the structure of the product has been detected, excepting in the case of benzaldehyde quoted below, which, however, cannot be regarded as being in any way analogous. It is, moreover, significant that in every case investigated the aldehydes gave open-chain amides and the ketones ring-compounds. It is clear that the matter requires further investigation.

We were unable to induce aromatic aldehydes to yield derivatives of glutaric acid by condensing them with cyanoacetamide. Guareschi, who has applied his reaction to a number of these aldehyes, found that the usual pyridine derivative (V) was formed at the expense of the normal condensation product (VI), which was itself reduced to the substance VII:

$$CPh{<}{\begin{matrix}C(CN)\cdot C(OH)\\C(CN){:}C(OH)\end{matrix}}{>}N \qquad CHPh{:}C(CN)\cdot CO\cdot NH_2$$

(V.) (VI.)

$$CH_2Ph\cdot CH(CN)\cdot CO\cdot NH_2$$

(VII.)

As a matter of fact the products in the case of benzaldehyde and cyanoacetamide depend on the conditions. Thus, if alcohol is used and a clear solution is maintained throughout, the products V and VII are formed in molecular proportions. If, however, no alcohol is used and the aldehyde is shaken with an aqueous solution of the amide, the sole product is the unsaturated compound (VI). Compound VI is also the sole product if alcohol is used and if the mixture is first seeded with a crystal of the unsaturated amide.

There appears to be no tendency whatever for an aromatic aldehyde to combine with two molecules of cyanoacetamide, and the glutaric acids having an aromatic group in the β-position cannot therefore be prepared by this method.

EXPERIMENTAL.

General Remarks.—Cyanoacetamide was prepared by the method described by Thole and Thorpe (T., 1911, **99**, 429). After recrystallisation from alcohol it was dried in the steam oven for three hours in order to remove traces of ammonia, a substance which has been found to have a marked hindering effect on condensations of this character.

The condensations were carried out in wide-mouthed, glass-stoppered bottles, the cyanoacetamide being dissolved in five times its weight of water. In some cases in which the heat generated by the reaction necessitated cooling in ice-water, thus causing the precipitation of some cyanoacetamide, a little more water was added in

order to effect complete solution. The aldehydes were fractionated immediately before use and were added to the cooled solution of cyanoacetamide, sufficient alcohol being added, when necessary, to form a clear solution. The condensing agents used were piperidine, diethylamine, and aqueous potassium hydroxide. No difference was noticed between these reagents when comparative experiments were carried out under similar conditions, and, therefore, a small quantity of a 50 per cent. aqueous solution of potassium hydroxide was invariably used.

Acetaldehyde.

αα'-Dicyano-β-methylglutaramide, $CHMe[CH(CN)\cdot CO\cdot NH_2]_2$.—This substance is produced in a yield approximating to 95 per cent. of that theoretically possible when 25·2 grams of cyanoacetamide dissolved in 126 c.c. of water are mixed with 6·6 grams of acetaldehyde and 0·3 c.c. of a 50 per cent. aqueous solution of potassium hydroxide added. Precipitation commences after about ten minutes and is complete at the end of three hours, when the material can be collected. The white, crystalline substance melts in the crude condition at 150—155° to a clear, yellow liquid, but owing to its insolubility it cannot be recrystallised from any of the usual solvents. The specimen for analysis was purified by being first ground with dilute hydrochloric acid and then washed with hot absolute alcohol. It melted sharply at 161° (Found, C=49·60; H=5·34; N=28·92. $C_8H_{10}O_2N_4$ requires C=49·48; H=5·19; N=28·87 per cent.).

β-Methylglutaric Acid.—This acid is produced from the amide in practically quantitative yield when 20 grams of the latter are warmed with 50 c.c. of concentrated hydrochloric acid, and the clear solution, after being diluted with an equal volume of water, is boiled for five hours.

The acid, in a very pure condition, can be extracted from the cooled solution by means of ether, and melts at 87° after being recrystallised from benzene or from dilute hydrochloric acid (Knoevenagel, *Ber.*, 1898, **31**, 2585) (Found, C=49·17; H=6·93. Calc., C=49·3; H=6·9 per cent. Silver salt, Found, Ag=59·87. Calc., Ag=59·95 per cent.).

6-Imino-3-cyano-5-carbamyl-4-methyl-2-piperidone,

$$CHMe{<}{\begin{matrix}CH(CN)\text{———————}CO\\ CH(CO\cdot NH_2)\cdot C(:NH)\end{matrix}}{>}NH,$$

can be obtained in small amount (about 0·25 per cent.) when the hydrochloric acid washings from the amide are treated with sodium acetate solution. It separates from water in small, colourless prisms, melts and decomposes at 235°, and is readily soluble in dilute hydrochloric acid. Crystallisation has to be effected rapidly, other-

wise some hydrolysis ensues (Found, C=49·72; H=5·39; N=28·77. $C_8H_{10}O_2N_4$ requires C=49·5; H=5·2; N=28·9 per cent.).

The compound is hydrolysed to β-methylglutaric acid by means of sulphuric acid (compare T., 1911, **99**, 431).

3-*Cyano*-2:6-*diketo*-4-*methylpiperidine*-5-*carboxylamide*,

$$CHMe<\begin{matrix}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot CO\end{matrix}>NH,$$

is formed by the action of hot dilute hydrochloric acid on the imino-compound (*loc. cit.*). It crystallises from water in colourless prisms which melt and decompose at 245° (Found, N=21·44. $C_8H_9O_3N_3$ requires N=21·5 per cent.).

The compound is completely converted into β-methylglutaric acid on hydrolysis with sulphuric acid.

When the original filtrate from the above condensation products is acidified by mixing it with one-third of its volume of concentrated hydrochloric acid a crystalline precipitate is formed which melts after recrystallisation from dilute hydrochloric acid at 252°, decomposing at 255° (Found, N=24·1. $C_8H_5O_2N_3$ requires N=24·0 per cent.). The yield of this substance was not more than 0·3 per cent. It is evidently 3:5-dicyano-2:6-dihydroxy-4-methylpyridine, $CMe<\begin{matrix}C(CN)\cdot C(OH)\\C(CN):C(OH)\end{matrix}>N$, described by Quenda (*Atti R. Accad. Sci. Torino*, 1896—1897, **32**, 415).

Propaldehyde.

αα′-*Dicyano*-β-*ethylglutaramide*, $CHEt[CH(CN)\cdot CO\cdot NH_2]_2$.—This substance separates in a crystalline condition when an aqueous solution containing 16·8 grams of cyanoacetamide, 120 c.c. of water, and 5·8 grams of propaldehyde is treated with 0·3 c.c. of a 50 per cent. solution of potassium hydroxide. The yield of the crude product is 90 per cent. of that theoretically possible. When purified by grinding with hydrochloric acid and recrystallisation from a mixture of alcohol and benzene it forms colourless needle clusters which melt at 147°. The compound is insoluble in dilute hydrochloric acid, and is only sparingly soluble in the usual organic solvents (Found: C=52·67; H=5·63; N=26·95. $C_9H_{12}O_2N_4$ requires C=51·9; H=5·8; N=26·9 per cent.).

β-*Ethylglutaric Acid.*—The above amide is converted into this acid on being boiled for five hours with dilute hydrochloric acid. It melts at 73° after recrystallisation from dilute hydrochloric acid (Emery, *Annalen*, 1897, **295**, 94) (Found, C=52·71; H=7·64. Calc., C=52·5; H=7·6 per cent. Silver salt, Found, Ag=57·55. Calc., Ag=57·7 per cent.).

6-Imino-3-cyano-5-carbamyl-4-ethyl-2-piperidone,

$$CHEt<\begin{matrix}CH(CN)\text{———————}CO\\CH(CO\cdot NH_2)\cdot C(:NH)\end{matrix}>NH,$$

occurs to the extent of about 0·5 per cent. in the original condensation, and can be isolated from the hydrochloric acid washings from the main product on treatment with aqueous sodium acetate. It separates from water in small crystals melting and decomposing at 214° (Found, N = 26·86. $C_9H_{12}O_2N_4$ requires N = 26·9 per cent.).

The compound is readily soluble in dilute hydrochloric acid.

3-Cyano-2 : 6-diketo-4-ethylpiperidine-5-carboxylamide,

$$CHEt<\begin{matrix}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot CO\end{matrix}>NH,$$

is produced in a crystalline condition when the above piperidone base is dissolved in dilute hydrochloric acid and the solution boiled for a few minutes. It separates in small, colourless prisms which, when recrystallised from water, melt and evolve gas at 236° (Found, N = 20·06. $C_9H_{11}O_3N_3$ requires N = 20·1 per cent.).

Both the above compounds are converted into β-ethylglutaric acid on hydrolysis.

n-*Butaldehyde.*

αα'-Dicyano-β-propylglutaramide, $CHPr^a[CH(CN)\cdot CO\cdot NH_2]_2$.—A yield of this substance representing 90 per cent. of that theoretically possible is produced when a solution containing 25·2 grams of cyanoacetamide, 180 c.c. of water, and 10·8 grams of *n*-butaldehyde is treated with 0·3 c.c. of an aqueous solution of potassium hydroxide. Precipitation is complete inthe course of three hours, and purification can be effected by grinding with dilute hydrochloric acid and crystallising from a mixture of alcohol and benzene. It forms a white, microcrystalline powder which melts at 136° (Found, C = 54·17; H = 6·30; N = 25·35. $C_{10}H_{14}O_2N_4$ requires C = 54·00; H = 6·4; N = 25·2 per cent.).

The compound is insoluble in hydrochloric acid.

β-Propylglutaric Acid, $CHPr^a(CH_2\cdot CO_2H)_2$.—The hydrolysis of the amide (25 grams) is best effected by means of a solution containing 70 c.c. of concentrated hydrochloric acid diluted with 100 c.c. of water, and is complete after having been boiled for five hours. The acid can be isolated by extraction with ether and purified by recrystallisation from hydrochloric acid, when it is obtained in small, needle-shaped crystals melting at 52° (Found, C = 55·04; H = 8·22. $C_8H_{14}O_4$ requires C = 55·2; H = 8·1 per cent.).

The acid is freely soluble in all the usual organic solvents and

in water. The *silver* salt is a white, apparently amorphous powder (Found, Ag=55·55. $C_8H_{12}O_4Ag_2$ requires Ag=55·6 per cent.).

The *anhydride*, $CHPr<\substack{CH_2\cdot CO\\CH_2\cdot CO}>O$, prepared from the acid through the agency of acetyl chloride, is a colourless, mobile liquid boiling at 180°/20 mm. (Found, C=61·24; H=7·68. $C_8H_{12}O_3$ requires C=61·5; H=7·8 per cent.).

The *semianilide*, $CHPr^a(CH_2\cdot CO\cdot NHPh)\cdot CH_2\cdot CO_2H$, from a benzene solution of the anhydride and aniline, crystallises from benzene in small, colourless plates melting at 128° (Found, N=5·86. $C_{14}H_{19}O_3N$ requires N=5·6 per cent.).

The *diethyl* ester, $CHPr^a(CH_2\cdot CO_2Et)_2$, prepared from the acid by means of alcohol and sulphuric acid, is a colourless oil which boils at 132°/10 mm. (Found, C=62·81; H=9·62. $C_{12}H_{22}O_4$ requires C=62·6; H=9·6 per cent.).

6-*Imino-3-cyano-5-carbamyl-4-propyl-2-piperidone*,

$$CHPr^a<\substack{CH(CN)\text{---------}CO\\CH(CO\cdot NH_2)\cdot C(:NH)}>NH.$$

—This substance is precipitated in a crystalline condition when the hydrochloric acid washings from the amide (p. 1471) are treated with sodium acetate solution. It separates from alcohol in small, prismatic crystals melting and decomposing at 208° (Found, N=25·95. $C_{10}H_{14}O_2N_4$ requires N=25·2 per cent.).

The compound is readily soluble in dilute hydrochloric acid.

3-*Cyano-2:6-diketo-4-propylpiperidine-5-carboxylamide*,

$$CHPr^a<\substack{CH(CN)\text{------}CO\\CH(CO\cdot NH_2)\cdot CO}>NH,$$

separates, on cooling, from a solution of the piperidone derivative in dilute hydrochloric acid after it has been boiled for five minutes. It separates from water in small, colourless needles melting at 229° with effervescence (Found, N=18·62. $C_{10}H_{13}O_3N_3$ requires N=18·8 per cent.).

The two last-named substances are each converted into β-propylglutaric acid on complete hydrolysis with sulphuric acid.

Benzaldehyde.

The conditions governing the course of the reaction between cyanoacetamide and benzaldehyde are discussed on p. 1468. The practical details are as follows.

(1) *Condensation in the Presence of Alcohol without Seeding.*—Cyanoacetamide (25 grams) dissolved in 126 c.c. of water is mixed with 16 grams of benzaldehyde and sufficient alcohol added (usually

about 90 c.c.) to give a clear solution. The addition of the usual amount of concentrated aqueous potassium hydroxide failed to produce any precipitation, and the solution was therefore kept for three days at 38—40°. Extraction with ether then yielded a solid material which crystallised from dilute alcohol in needles melting at 129—130° (Found, C=68·77; H=5·80; N=16·29. Calc., C=68·9; H=5·7; N=16·1 per cent.).

The compound was proved to be identical with α-cyano-β-phenylpropionamide, $CH_2Ph\cdot CH(CN)\cdot CO\cdot NH_2$, by direct comparison with a specimen of this substance prepared by Hessler's method (*Amer. Chem. J.*, 1899, **22**, 169) by the action of benzyl chloride on the dry sodium compound of ethyl cyanoacetate.

When the aqueous solution left after extraction with ether in the above experiment is acidified with hydrochloric acid a white precipitate is formed, which crystallises from alcohol or, better, from dilute hydrochloric acid in needle clusters melting and decomposing at 245° (Found, C=65·6; H=3·28; N=17·93. Calc., C=65·8; H=2·9; N=17·7 per cent.). The compound is evidently 3:5-dicyano-6-hydroxy-4-phenyl-$\Delta^{3,6}$-dihydro-2-pyridone,

$$CPh{<}\begin{matrix}C(CN)\text{———}CO\\CH(CN)\cdot C(OH)\end{matrix}{>}N,$$

originally prepared by Guareschi (*Atti R. Accad. Sci. Torino*, 1898—1899, **34**, 565) by the action of ammonia on a mixture of benzaldehyde and ethyl cyanoacetate. Guareschi describes his compound as crystallising with $3H_2O$, but a direct comparison of the two compounds left no doubt as to their identity. The substance is remarkable in that it is freely soluble in cold water and will crystallise from this solvent in the hydrated form described by Guareschi if the solution is sufficiently concentrated.

If, however, a small quantity of hydrochloric acid is added to the aqueous solution, the compound immediately separates in the anhydrous condition. The relative amounts of the two compounds formed in the above condensation are approximately in the proportion of their molecular weights, namely, 10 grams of the amide to 16·5 grams of the pyridine derivative.

(2) *Condensation without Alcohol.*—The same quantities were used as in the previous experiment, only in this instance no alcohol was added. Vigorous shaking was necessary in the initial stages of the reaction, but the condensation product soon began to form, and the precipitation was complete after two hours. The compound produced in this way crystallised from benzene in clusters of silky needles melting at 123° (Found, C=69·55; H=4·73; N=16·63.

Calc., C = 69·7; H = 4·7; N = 16·3 per cent.), and was proved by direct comparison to be α-cyanocinnamamide,

$$CHPh:C(CN)\cdot CO\cdot NH_2,$$

and to be the same substance as that prepared by Heuck (*Ber.*, 1895, **28**, 2252).

(3) *Condensation in the Presence of Alcohol with Seeding.*—A yield of 80 per cent. of α-cyanocinnamamide in a pure, crystalline condition can be obtained in the course of two hours when a solution containing 16 grams of cyanoacetamide, 21 grams of benzaldehyde, 70 c.c. of alcohol, and 84 c.c. of water, which has been mixed with 0·3 c.c. of a 50 per cent. solution of potassium hydroxide in water, is seeded with a crystal of the unsaturated amide.

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Organic Chemistry.

Oxidation of Hydrocarbons by Oxygen. Oxidation of Paraffin. C. Kelber (*Ber.*, 1920, **53**, [*B*], 1567—1577. Compare Fischer and Schneider, this vol., i, 519; Grün, this vol., i, 520).—In a previous communication (this vol., i, 280), the author has dealt with the volatile acids obtained by the oxidation of paraffin; he now describes the investigation of the residual mass, which amounts to 90—100% of the initial material, and has iodine number 1—2, saponification number 250—300, and acid number about 200. The highly complex mixture of acids cannot be separated into its components by the ordinary methods, and only by a suitable combined process is it possible to isolate and identify certain acids. At present, efforts have been mainly directed towards the characterisation of solid, saturated, normal fatty acids from $C_{10}H_{20}O_2$ onwards, such as occur in the animal and vegetable organisms.

The crude residue is washed with water and then hydrolysed with alkali hydroxide; after removal of unsaponifiable matter, the acids are liberated, and a fraction soluble in light petroleum is prepared. This fraction is esterified with ethyl alcohol, and a partial separation is effected by distillation of the ethyl esters under diminished pressure. The ester fractions are separately hydrolysed, and the resulting acids are separated by suitable combinations of the following methods: (i) crystallisation of the acids, (ii) separation of the potassium salts by acetone (compare Fuchini and Dorta, A., 1914, ii, 153), (iii) the magnesium acetate method, and (iv) crystallisation of a mixture containing a suspected acid from a saturated solution of that acid. The presence of the following acids has so far been established: decoic, myristic, palmitic, heptadecoic, stearic, and arachidic, and an acid, $C_{16}H_{32}O_2$, which is isomeric with palmitic and possibly identical with Bergmann's *iso*palmitic acid (A., 1918, i, 285).

H. W.

The Chlorination of Ethylene in the Presence of Calcium Chloride. J. A. Smythe (*Gas J.*, 1920, **149**, 691—693).—A simple apparatus is described for use with Newth's method (T., 1901, **79**, 915) for the preparation of ethylene, by means of which a steady supply of the pure gas may be obtained. When the gas prepared in this way is passed, along with chlorine, over a short layer of calcium chloride in a water-cooled tube, a mixture of dichloroethane (50%), trichloroethane (25%), and less volatile compounds (25%) is obtained, and from this pure dichloroethane may readily be separated by fractionation. The trichloroethane probably results from the secondary action of chlorine on the dichloroethane, and not from the preliminary formation of vinyl chloride with subsequent addition of chlorine. The less volatile compounds are probably chloro-derivatives of polymerides of ethylene.

Dichloroethane behaves towards potassium carbonate in a precisely similar manner to dibromoethane, giving ethylene glycol and vinyl chloride, but the action is much slower than with the dibromoethane. W. G.

The Interaction of Ethylene and Sulphuryl Chloride. WILLIAM FOSTER (*Science*, 1920, **51**, 641—642).—At the ordinary temperature, no apparent change occurs when ethylene is bubbled through sulphuryl chloride. Under certain conditions, not mentioned, on continued passage of the gas the solution becomes greenish-yellow, and the temperature rises to a maximum of 35—40°. Then the solution becomes colourless, the temperature falls, and the colour reappears. This cycle is repeated often, each time becoming longer and the temperature differences less pronounced. Some products of the reaction are ethylene dichloride and sulphur dioxide. The subject is still under investigation.

CHEMICAL ABSTRACTS.

Preparation and Characterisation of Ethylenebromohydrin. JOHN READ and REXFORD GEORGE HOOK (T., 1920, **117**, 1214—1226).

Preparation of *iso*Amyl Alcohol by Pasteur's Method. FÉLIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 220—226).—In the preparation of the amylsulphuric acids, which is the first step in the isolation of pure *iso*amyl alcohol from fusel oil by the fractional crystallisation of the barium amylsulphates, the best results are obtained with 90—91% sulphuric acid (D 1·820—1·825), using an excess of 15—20% above the theoretical quantity. Under these conditions, about 60% of the alcohol is esterified, but as a small proportion is apparently converted into the normal sulphate, the actual yield of the acid sulphates amounts to about 50—55%. If a large excess of sulphuric acid is used, considerable difficulties are encountered later in the separation of the barium sulphate without any adequate compensation in the increased percentage of alcohol esterified. G. F. M.

[Reactions and Derivatives of ββ'-Dichlorodiethyl Sulphide.] O. B. HELFRICH (*J. Amer. Chem. Soc.*, 1920, **42**, 1839).—The author states that certain of the physical constants (this vol., i, 525) previously given are incorrect. The following are the corrected values: Line 24,* read "b. p. 222—223°/21 mm." Line 20,* "m. p. 171°." Line 17,* "b. p. 173—175°/21 mm." Line 13,* "b. p. 193—195°/22 mm." W. G.

Catalytic Reduction of Organic Compounds with the Aid of Nickel Carbonyl. RUDOLF LESSING (D.R.-P. 321938; from *Chem. Zentr.*, 1920, iv, 367).—(1) The catalyst is brought into action at the moment of decomposition of the nickel carbonyl. (2) The nickel carbonyl and hydrogen or gases, which are richer in hydrogen than technical water-gas, are brought into contact with the substance to be hydrogenated at a suitable temperature

* From bottom.

during the whole course of hydrogenation. (3) The nickel carbonyl is dissolved in the substance under treatment, and the solution is injected into a heated vessel, in which it comes into contact with hydrogen or the hydrogenating agent.

Hydrogen containing 5—10% of carbon monoxide is used in the treatment of oils or fatty acids. The more volatile tar oils, benzene, etc., are heated to the requisite temperature with hydrogen containing nickel carbonyl; the preparation of aniline from nitrobenzene is effected similarly. H. W.

Keto-enolic Desmotropy. XII. The Fractional Distillation of Ethyl Acetoacetate. KURT H. MEYER and VIKTOR SCHOELLER (*Ber.*, 1920, **53**, [*B*], 1410—1416).—Ethyl acetoacetate has been distilled from a Jena-glass apparatus which had been cleaned by being steamed, washed with alcoholic hydrogen chloride, and dried at 100°. The operation was performed under 2 mm. pressure, and the ester was thus divided into four equal fractions and a residue in the flask; the former contained 78%, 76%, 72%, and 63%, respectively, of the enolic form, of which only 5% was present in the residue. The whole distillate is highly enolised, whilst an ester richer in the ketonic form remains in the flask. Special experiments show that enolisation only occurs to a slight extent in the vaporous phase, even when this is superheated and in contact with glass. The change seems to be mainly located on the walls of the neck of the flask and the column, where the condensed ketone, in boiling, is isomerised to the equilibrium ester, which evolves the more volatile enolic form. Since the desmotropic change was probably due to the catalytic action of the glass, the experiment was repeated, using a quartz flask with glass condenser and receivers; the enolic contents of three fractions and a residue, all of equal volume, were 22, 11, 2·5, and 0% respectively. The mean percentage of enol in distillates and residue combined was 8·9%, so that the ester was practically unaffected by the distillation. It appears beyond doubt that fractionation under "aseptic" conditions affords the readiest means of isolating the pure ketone, and the enolic form may also be isolated by repeated distillation of larger amounts. (The enolic content of the various fractions is deduced from their refractive indices, a graph showing the relationship between the two functions being given in the original.)

Methyl benzoylacetate has been similarly distilled from a glass flask; three successive fractions contained 40, 21, and 20% of the enolic form, which was present to the extent of 8% in the residue and 18% in the original ester. In this experiment, it is noteworthy that the first drops of the distillate solidified in the condenser, a sign of the presence of the almost pure enolic form. H. W.

Decomposition of the Acid Salts of Dibasic Acids in Aqueous Solution. V. TH. SABALITSCHKA (*Ber.*, 1920, **53**, [*B*], 1383—1387. Compare A., 1919, i, 433, and previous abstracts).—Aqueous solutions of the potassium hydrogen salts of malonic,

succinic, maleic, and fumaric acids have been extracted with ether, and the amount of acid removed has been determined; the partition-coefficient of the free acids between ether and water has been measured under identical conditions. The ethereal solution was found to contain about one-thirteenth of the malonic acid originally present in the acid salt, whilst the corresponding fractions for succinic and fumaric acids are one-sixth and one-fifth; further, the presence of free acid in the aqueous solution of the hydrogen maleate could not be detected. Protracted continuous extraction of an aqueous solution of potassium hydrogen succinate by ether showed that it is possible to remove nearly the whole of the acid portion by this means, but the process becomes very slow towards the end, partly by reason of the diminished concentration of the free acid in the aqueous solution, but also in consequence of the presence of relatively large quantities of normal salt. H. W.

The Electrosynthetic Preparation of *n*-Tetradecane-αω-dicarboxylic Acid. KARL STOSIUS and KARL WIESLER (*Biochem. Zeitsch.*, 1920, **108**, 75—81).—On electrolysing the potassium ethyl ester of azelaic acid, ethyl *n*-tetradecane-αω-dicarboxylate was obtained: $2CO_2Et\cdot[CH_2]_7\cdot CO_2K = CO_2Et\cdot[CH_2]_{14}\cdot CO_2Et + 2CO_2 + 2K$. From this the acid was obtained, and found, as expected, to be identical with thapsic acid, isolated by Canzoneri from juniper berries (A., 1884, 461). S. S. Z.

The Growth of Crystals of Potassium Sodium Tartrate. MISHIO ISHIMOTO (*Proc. Phys.-Math. Soc. Japan*, 1920, [3], **2**, 81). —The crystals of potassium sodium tartrate were obtained from the solution by very slow cooling. Successful growth depends on the rate of cooling and the evaporation of the liquid. The solution was kept in a 25-litre thermostat heated electrically. The vessel containing the solution was sealed practically air-tight to retard the evaporation of the liquid. The solution was prepared to be saturated at a temperature between 30° and 32°, and its rate of cooling was slow, about 0·2—0·4° per day. In such a way, crystals of 6—7 cm. in length were obtained in two weeks or more.
CHEMICAL ABSTRACTS.

Production of Saccharic Acid and Tartaric Acid from Carbohydrates. DIAMALT AKT.-GES. (Brit. Pat. 108494).—Saccharic and tartaric acids are readily obtained by oxidising carbohydrates with sulphuric and nitric acids, or sulphuric acid and oxides of nitrogen, peroxidised by treatment with air, ozone, or oxygen, at a temperature of 100°, in presence of oxidising catalysts, particularly molybdenum, mercury, or platinum. For example, 100 parts of starch are mixed with 150 parts of water and 3 parts of sulphuric acid and saccharified. Concentrated sulphuric acid (25 parts), nitric acid (D 1·4; 60 parts), and an oxide of molybdenum (1 part) are then added, and the reaction mixture is maintained at 100°, a further 100—140 parts of nitric

acid being gradually introduced. At the end of the operation, the nitric acid is evaporated, and, after diluting the residual liquor with water, the molybdenum is precipitated by hydrogen sulphide and the sulphuric acid and traces of oxalic acid by lime or baryta, and saccharic acid separated from the filtrate, after concentration, as potassium hydrogen saccharate. The yield amounts to 65%. If mercury is used as catalyst, and twice the quantity of nitric acid is added, a yield of 60% of potassium hydrogen tartrate, together with about 10% of saccharate, is obtained. G. F. M.

Mixed Dismutation of Aldehydes. F. F. NORD (*Biochem. Zeitsch.*, 1920, **106**, 275—280).—The reaction between two different aldehydes, expressed by the equations $R\cdot CHO + R_1\cdot CHO + H_2O = R\cdot CH_2\cdot OH + R_1\cdot CO_2H$ or $R_1\cdot CH_2\cdot OH + R\cdot CO_2H$, is termed mixed dismutation of aldehydes. According to Neuberg's theory of fermentation (Neuberg and Kerb, A., 1914, i, 118), such a reaction may be assumed to take place between the two intermediate products, methylglyoxal and acetaldehyde, in such a way that pyruvic acid and ethyl alcohol are formed until all the sugar is exhausted:

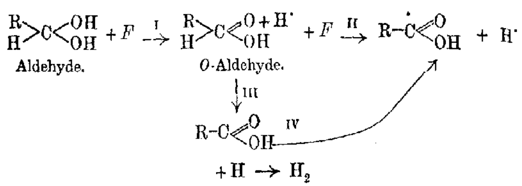
$$\begin{matrix} CH_3\cdot CO\cdot CHO \\ CH_3\cdot CHO \end{matrix} + \begin{matrix} O \\ | \\ H_2 \end{matrix} = \begin{matrix} CH_3\cdot CO\cdot CO_2H \\ CH_3\cdot CH_2\cdot OH \end{matrix}.$$

The author has investigated the reactions between the following pairs of aldehydes in presence of aluminium ethoxide as condensing agent: (1) acetaldehyde and *iso*valeraldehyde, (2) *iso*valeraldehyde and benzaldehyde, and (3) acetaldehyde and benzaldehyde. In each case, mixed dismutation occurs, the products in case (1), for instance, being ethyl acetate, amyl valerate, amyl acetate, and ethyl valerate. T. H. P.

The Dehydroxidation of Aldehydes. Mechanism of Oxidation. ERICH MÜLLER (*Annalen*, 1920, **420**, 241—261. Compare Müller and Hochstetter, A., 1914, ii, 615; Fichter, A., 1918, ii, 439).—It has been shown that when an alkaline solution of formaldehyde is electrolysed with a copper anode, equal volumes of hydrogen are initially evolved from either pole, but the evolution from the anode gradually ceases as the electrolysis proceeds: it is now found that the process occurs for an indefinite period when the anode is made of copper foil which has been covered with molten cuprous chloride and subsequently cathodically reduced in sodium hydroxide solution, or of silver foil which has been treated in a similar manner. A similar action takes place in the presence of certain metallic oxides, of which cuprous and cupric oxides, as well as silver oxide, have been particularly investigated; in these cases there is a period of incubation. The reaction has been extended to acetaldehyde and benzaldehyde, which are also found to be converted into the corresponding acid and gaseous hydrogen. The latter is also evolved in small quantity from alkaline solutions of formaldehyde in the presence of certain metals and in the

absence of particular oxidising agents; these metals also catalytically accelerate the Cannizzaro reaction.

The mechanism of oxidation is represented by the following scheme:



in which F is the charge induced by the electric current or by an oxidising agent. The primary product of the oxidation of an aldehyde is the corresponding O-aldehyde; dehydroxidation occurs if this is more readily oxidised according to III than in accordance with II. Conversion of aldehyde into acid without evolution of hydrogen may occur along the lines I and II, or I, III, and IV. Whether or not hydrogen is evolved during the oxidation of the aldehyde in the presence of catalysts depends on whether the latter accelerate III more than IV. H. W.

Quantitative Investigation of Cannizzaro's Reaction in the Condensation of Acetaldehyde by Aqueous Alkalis. HARALD HAMMARSTEN (*Annalen*, 1920, **420**, 262—275).—The investigation forms part of a biochemical study of the function of acetaldehyde in plants. Under the action of aqueous alkali, the aldehyde is decomposed into alcohol and acid, into aldol and aldehyde resin. The first and third types of action are chiefly described in the present communication.

The experiments were carried out with $N/2$-aqueous acetaldehyde solution at 0°, 18°, and 50° respectively. The bases used were the hydroxides of potassium, barium, calcium, and lead. In addition, buffer solutions prepared from the di- and monohydrogen phosphates of potassium and sodium, and from borate and sodium hydroxide, were also employed. In the case of the alkali hydroxide solutions, the amount of acid formed was estimated by titration of the resulting solution with acid in the presence of phenolphthalein, with the buffer mixtures, the solutions were strongly acidified with phosphoric acid, distilled to syrupy consistency, and subsequently treated with steam until all acetic acid was removed, the latter being then titrated in the combined distillate. Aldehyde resin was estimated by extraction of the solutions with chloroform, evaporation of the latter, and desiccation of the residue at 120°/10 mm. until constant in weight.

The results are given in an extended series of tables. It is found that the aldol condensation proceeds at a relatively much greater rate than the Cannizzaro reaction, the former taking place

so rapidly that it is impossible for any considerable amounts of alcohol or acid to be formed. The maximum production of acid observed during the whole course of the experiments is only 12·5% of that theoretically possible. H. W.

Additive Compounds of the Acetylacetone Derivatives of the Rare Earths. G. JANTSCH and E. MEYER (*Ber.*, 1920, **53**, [*B*], 1577—1587. Compare Biltz and Clinch, A., 1904, i, 715.)—A series of additive compounds of the acetylacetone derivatives of the rare earths with ammonia, aniline, and pyridine has been investigated in the hope that a convenient chemical means of separating these elements might be found in their internally complex salts or their additive compounds. This does not, however, appear to be the case. The compounds which are described are considered to be constituted according to the annexed general formula.

$$\left[M\left(\begin{matrix} O\cdot CMe \\ >CH \\ O\!:\!CMe \end{matrix}\right)_3\right]\ldots R$$

Lanthanum acetylacetone, m. p. 151° (Biltz, *loc. cit.*, gives 183°), combines with a molecule of ammonia, pyridine, or aniline, respectively, to yield *compounds*, colourless needles, m. p. 147·5°, slender, colourless needles, m. p. 142°, and colourless, silky needles, m. p. 192°. *Lanthanum dibenzoylmethane*, pale yellow, shining needles, m. p. 141—143°, is obtained by the action of dibenzoylmethane on a suspension of lanthanum hydroxide in boiling ethyl alcohol; it combines with a molecule of ammonia, yielding a *substance*, pale yellow, slender needles, m. p. 99°, which rapidly loses the whole of the ammonia on exposure to air. Gadolinium acetylacetone is isolated in the form of the *dihydrate*, which, when crystallised from absolute alcohol, passes into the *monohydrate*, colourless, transparent needles, m. p. 142°; the *pyridine* compound, $Gd(C_5H_7O_2)_3,C_5H_5N$, forms colourless needles, m. p. 139·5°. *Yttrium acetylacetone*, colourless, transparent, pointed needles, m. p. 131°, is prepared in the same manner as the lanthanum salt, than which it is considerably more stable; the *compounds* with ammonia, pyridine, aniline, and acetonitrile form colourless needles, m. p. 129°, slender, shining needles, m. p. 121°, small needles, m. p. 109°, and colourless, fatty crystals, m. p. 138°; the first- and last-named compounds are somewhat unstable. *Yttrium dibenzoylmethane* forms long, yellow, shining needles, m. p. 240°; it does not appear to yield additive compounds with ammonia, pyridine, aniline, or acetonitrile. H. W.

Mutarotation of Dextrose in Alkaline Solution. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1920, **106**, 23—36).—The author has measured the velocities of disappearance of the mutarotation of dextrose in distilled water and in $N/10$—$N/7000$-sodium carbonate solutions, all the measurements being carried out at 20·4°. The values of the velocity constant of the change of mutarotation for different concentrations of sodium carbonate are: water, 7·11; $N/7000$, 7·32; $N/6000$, 9·32; $N/5000$, 12·70;

$N/2000$, 24·4; $N/1000$, 56·5; $N/500$, 93·1, these numbers giving almost exactly a straight line when plotted against the concentrations of the alkali (compare Osaka, A., 1909, i, 456). T. H. P.

The Stability of α-Dextrose. HANS VON EULER and ARVID HEDELIUS (*Biochem. Zeitsch.*, 1920, **107**, 150—158).—The H-ion concentration conducive to the maximum stability in the mutarotation of dextrose is $P_H = 3{\cdot}6 \pm 0{\cdot}2$. The temperature-coefficient at this H-ion concentration is only slightly higher than that at $P_H = 5$. S. S. Z.

Action of the Carbonates of the Alkaline Earths on Dextrose. III. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, **101**, 74—81. Compare this vol., i, 13, 662).—As in the case of calcium carbonate, strontium carbonate, barium carbonate, and magnesium carbonate when boiled with a solution of dextrose, gradually reduce the dextrorotation of the solution to zero or to slight lævorotation. The reduction of the sugar also falls, but to a smaller extent than the rotation. The formation of lævulose is established by the isolation of the phenylmethylosazone of this sugar from the treated solution. The fall in the reduction is ascribed to the formation of acids. The velocity of the change in the rotation is proportional to the equivalent weights of the dissolved substances. S. S. Z.

Rate of Hydrolysis of Phosphoric Esters of Sugar Derivatives. P. A. LEVENE and M. YAMAGAWA (*J. Biol. Chem.*, 1920, **43**, 323—338).—There is much evidence that the ester derivatives of sugar may show considerable differences in the rate at which they are hydrolysed. The substances studied in this work were the phosphoric esters of (1) α-methylglucoside; (2) βγε-trimethyl methylglucoside; (3) α-, β-, γ-, ε-diacetoneglucose; (4) αβ-monoacetone-glucose; (5) a phosphoric acid ester of the same sugar derivative as in (4), but differing in the position of the acid radicle; (6) ζ-benzoyl-αβ-monoacetone-glucose. The position of the phosphoric acid in the first compound is not known, but in (2) and (3) it is attached to the same carbon atom, so that these two compounds differ only in the nature of the substituent group. The fourth substance is formed as a by-product by the action of phosphoryl chloride on diacetone-glucose, and apparently contains the phosphoric acid radicle attached to a primary alcohol grouping, whereas the fifth substance is prepared by the action of phosphoryl chloride on monoacetone-glucose, and contains the phosphoric acid linked to a secondary alcohol group. The sixth substance differs from the preceding two by containing the phosphoric acid in a different position, by the number of the substituting groups, and by the difference in character of one of these groups.

The hydrolysis of these six substances was studied in approximately equivalent concentration, which was in the neighbourhood of

10%. The condition of hydrolysis consisted of treatment with $0.1N$-sulphuric acid at 100°. The rate of hydrolysis followed the unimolecular law, and the following constants were obtained: K_1, $22(10^{-3})$; K_2, $43(10^{-3})$; K_3, $56(10^{-3})$; K_4, $44(10^{-3})$; K_5, $58(10^{-3})$; K_6, $18(10^{-3})$.

These results indicate that both the position of the phosphoric acid radicle and the character of the substituent groups exert an influence on the stability of the ester linking. J. C. D.

Crystalline Chlorotetra-acetyllævulose and Related Derivatives. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1920, **42**, 1846—1854).—β-Penta-acetyllævulose, when shaken in chloroform solution with aluminium chloride and phosphorus pentachloride, gives *chlorotetra-acetyllaevulose*, m. p. 83°, $[\alpha]_D^{20}$ −160·9°, which slowly decomposes in the air, giving tetra-acetyllævulose. By its general behaviour it is probable that this compound is an α-derivative. A better yield of the compound is obtained if the tetra-acetate is used instead of the penta-acetate, whilst if aluminium chloride is omitted in the preparation, the main product is *β-chlorotetra-acetyllaevulose*, m. p. 108°, $[\alpha]_D^{20}$ +45·3°. On ethylation, tetra-acetyllævulose gives *β-ethyltetra-acetyllaevulose*, m. p. 83°, $[\alpha]_D^{20}$ −127·6°. *β-Ethyl laevuloside*, m. p. 151°, $[\alpha]_D^{20}$ −155·3°, was obtained by the process previously described for β-methyl lævuloside (compare A., 1916, i, 547). Attempts to prepare α-methyl lævuloside by a biochemical method or by Fischer's method (compare A., 1895, ii, 553) were not successful. W. G.

Action of Different Catalysts on the Combustion of Burning Sucrose. J. ARVID HEDVALL (*Svensk. Kem. Tidskr.*, 1920, **32**, 99—103; from *Chem. Zentr.*, 1920, iii, 337—338).—The author has extended the observations of Schade (*Münch. med. Woch.*, 1905, i, 1088) on the combustion of pieces of sucrose in air by distinguishing between the burning without formation of residue and that with the production of a porous mass, and by examining the effect of a large number of catalysts. The type of combustion first named is caused by strongly basic oxides and hydroxides, by certain oxides which are known to form complex organic compounds or to yield higher oxides transitorily, and by certain free metals. The formation of a residue occurs in the presence of free halogens, halogen hydracids, sulphuric acid, and certain other acids, and of many normal salts. H. W.

The Chemistry of Polysaccharides. The Preparation of Pure Polysaccharides. The Mode of Action of Diastatic Enzymes and the Dextrin Stage of Polysaccharides. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1920, **107**, 268—294).—Pure starch was prepared by digesting fresh plant tissue with 33% sodium hydroxide on the water-bath, and by precipitating with 90% alcohol after centrifuging off the insoluble constituents. The precipitate was dissolved in water and repre-

cipitated with 90% alcohol, this being repeated twice; it was finally neutralised with hydrochloric acid, and precipitated again with alcohol. The same method was employed in the treatment of yeast, and the insoluble portion obtained by centrifuging the product from the first digestion of the yeast with the alkali was treated again with boiling alkali and alcohol, which yielded a cellulose-like substance. Cellulose was prepared from cotton wool by digesting it with strong sodium hydroxide and small quantities of carbon disulphide, centrifuging, and precipitating the viscous fluid with 90% alcohol. It was purified by reprecipitation with alcohol and neutralised with hydrochloric acid. Agar was purified by precipitating an alkaline solution of it with alcohol. Glycogen was obtained by digesting minced liver with 33% sodium hydroxide, and was purified by precipitation with alcohol. The properties of the polysaccharides prepared by the above methods were studied. The theory of the iodine reaction and of the action of diastatic enzymes as explained from considerations of the condition of the dispersed colloidal particles of the polysaccharides is discussed.

S. S. Z.

A Compound of Starch with Phosphoric Acid. JOHANNES KERB (*Biochem. Zeitsch.*, 1919, **100**, 3—14).—Starch was esterified with phosphoric acid by treating a soluble preparation with a solution of phosphoryl chloride in chloroform in the presence of calcium carbonate. The calcium salt of the amylophosphoric acid was precipitated with alcohol from the concentrated solution and purified. By means of diastatic cleavage, hexose monophosphoric acid was obtained from the compound in the form of a calcium salt. The latter substance was fermented by yeast. S. S. Z.

Preparation and Properties of a Highly-oxidised Cellulose. EDMUND KNECHT and LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 251—255).—An improved method for preparing oxycellulose is carried out by treating filter paper with an acid solution of potassium permanganate (either one or two atoms of oxygen for each molecule of cellulose—$C_6H_{10}O_5$), washing the brown, disintegrated powder so formed, decolorising with hydrogen peroxide, and drying at 40°. In the stronger oxidation, the aldehyde group in the oxycellulose is not attacked. The method avoids the decomposition of oxycellulose by alkalis into non-reducing substances and its hydrolysis by acids. The so-formed oxycellulose gives an intense yellow colour with sodium hydroxide, and, on neutralisation, an acid cellulose having only slight reducing power is formed. It forms hydrazones with phenylhydrazine and *p*-nitrophenylhydrazine. On reduction, oxycellulose does not yield cellulose.

When kept for one day with cold 0·880 ammonia solution, a gelatinous mass is formed, which retains various amounts of ammonia on washing. Probably an unstable aldehyde–ammonia is formed. Oxycellulose does not react with aniline, but with hydrazine hydrate, hydroxylamine, and hydrogen cyanide it gives

indefinite compounds containing nitrogen. It reacts with sodium hydrogen sulphite solution.

Oxycellulose exerts its strongest reducing power in alkaline solution, and reduces solutions of cupric, silver and ferric salts. In the presence of sodium hydroxide, it readily reduces methylene-blue, safranine, rosinduline, indanthren, and indigotin.

It is not possible to estimate oxycellulose by means of its reaction with *p*-nitrophenylhydrazine, since absorption compounds are formed.

The new oxycellulose had a copper number of 14·2, as compared with 7·6 for Nastjukov's bleaching powder-oxycellulose.

A. J. H.

Picrates of the Nitrogen Bases of the Alcohol Radicles. A. RIES (*Zeitsch. Kryst. Min.*, 1920, **55**, 454—522. Compare T., 1909, **95**, 1275.)—Detailed crystallographic and optical data are given for thirty-one compounds, ranging from methylammonium picrate to tetra-*n*-propylammonium picrate. Many are dimorphous or trimorphous, whilst trimethyl*iso*propylammonium picrate is tetramorphous, and trimethyl*iso*butylammonium picrate is pentamorphous, namely, (1) monoclinic, D^{15} 1·378; (2) triclinic, D^{15} 1·378; (3) monoclinic-domatic, D^{15} 1·419; (4) triclinic, probably asymmetric, D^{15} 1·377; (5) hexagonal, D^{15} 1·377. Many are hexagonal or pseudo-hexagonal, or with prism-angles approaching 60°.

L. J. S.

Certain New Transformations of Ethylenediamine. WILHELM TRAUBE and ELISABETH PEISER (*Ber.*, 1920, **53**, [*B*], 1501—1508).—Aminoethylaminosulphonic acid (Traube and Brehmer, A., 1919, i, 434) has been converted into the corresponding nitroso-derivative, by the decomposition of which a series of hydroxy-, alkyloxy-, and halogeno-ethylamines has been prepared.

A well-cooled solution of β-aminoethylaminosulphonic acid in water is mixed with an aqueous solution of sodium nitrite, and subsequently acidified with dilute sulphuric acid, when *β-aminoethylnitrosoaminosulphonic acid*, $C_2H_4<\begin{smallmatrix}NH_3\\N(NO)\cdot SO_3\end{smallmatrix}>$, separates in well-defined crystals, which are extremely explosive when dry (the moist preparations are used in the following experiments). The acid decomposes quantitatively in boiling aqueous solution in accordance with the equation $NH_2\cdot CH_2\cdot CH_2\cdot N(NO)\cdot SO_3H + H_2O = NH_2\cdot CH_2\cdot CH_2\cdot OH + N_2 + H_2SO_4$, and the β-aminoethyl alcohol was identified as the picrate, m. p. 159°, and picrolonate, m. p. 225° (decomp.). Concentrated hydrochloric acid converts the nitroso-acid into β-chloroethylamine (the *sulphate* was analysed), whilst hydrobromic acid acts with such violence that explosions readily occur, and gives β-bromoethylamine. *β-Fluoroethylamine*, obtained by treatment of the nitroso-acid with 40% hydrofluoric acid, evaporation of the solution, and distillation of the residue with steam after addition of an excess of alkali, has a strong odour

of ammonia, and is distinguished from the remaining halogeno-ethylamines by the much greater firmness with which the halogen atom is retained. The *hydrochloride*, *hydrobromide*, and *nitrate* are crystalline salts, but are not very characteristic by reason of their hygroscopic nature and ready solubility; the *picrolonate* crystallises in yellow, non-hygroscopic needles, m. p. 239°.

β-Aminoethyl methyl ether, colourless, mobile liquid, b. p. 95°/756 mm., is prepared from the nitroso-acid and boiling absolute methyl alcohol; the *hydrochloride*, hygroscopic crystals, and the *picrolonate*, yellow needles, m. p. 235°, are described. β-Amino-diethyl ether (picrolonate, m. p. 204°) is prepared in a similar manner. β-Aminoethyl methyl ether hydrochloride is transformed by potassium cyanate solution into *β-carbamidoethyl methyl ether*, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot OMe$, m. p. 63° after softening at 61°. The aqueous solution of the base reacts with phenylcarbimide to give *phenylcarbamidoethyl methyl ether*, m. p. 94·5°. *β-Amino-ethyl* n-*propyl ether* was isolated in the form of its *picrolonate*, yellow, prismatic crystals, m. p. 188°, when rapidly heated.

The action of phenol on β-aminoethylnitrosoaminosulphonic acid leads to the formation of β-aminoethyl hydrogen sulphate instead of the expected aminoethyl phenyl ether. H. W.

Alkylimidodisulphonic Acids. WILHELM TRAUBE and MAX WOLFF (*Ber.*, 1920, **53**, [*B*], 1493—1501).—The investigation of the alkylation of basic potassium hydroxylaminedisulphonate (Traube, Ohlendorf, and Zander, this vol., i, 717) has been extended to basic potassium imidodisulphonate, $NK(SO_3K)_2$, which shows a somewhat similar behaviour, particularly towards the more active alkylating agents; with substances such as propyl iodide and benzyl chloride, the process is slower, the yields are poorer, and the products are mixed with potassium imidodisulphonate. The cause of this lies in the hydrolysis of the basic salt in aqueous solution, $NK(SO_3K)_2 + H_2O \rightleftharpoons NH(SO_3K)_2 + KOH$, and the dual nature of the process, which includes the alkylation of the basic salt and the decomposition of the alkyl haloid by free alkali; if the first process is slow and the second is comparatively rapid, equilibrium is so far disturbed by the removal of the alkali hydroxide that the normal salt is largely regenerated. Attempts to overcome this difficulty by working with concentrated solutions have not been particularly successful. The potassium alkylimidodisulphonates are readily decomposed by dilute acid into alkylamidosulphonates, which are then slowly converted into the corresponding primary amines.

Basic potassium imidodisulphonate is readily transformed by methyl sulphate or methyl iodide into *potassium methylimidodisulphonate*, $NMe(SO_3K)_2$, shining leaflets (the *lead*, *silver*, and *barium* salts dissolve freely in water), which is converted by very dilute sulphuric acid into *potassium methylamidosulphonate*, $NHMe\cdot SO_3K$, and by 25% hydrochloric acid into methylamine hydrochloride, the yield of the latter being 88% of that theoretically possible. Similarly, *potassium ethylimidodisulphonate*, long

needles, is converted into ethylamine (yield, 64%) and *potassium propylimidodisulphonate*, long, shining needles, into propylamine (yield about 40%). *Potassium epihydrinaminedisulphonate* is freely soluble in water.

Potassium ethylenediamine-NN′-*tetrasulphonate*,

$$C_2H_4[N(SO_3K)_2]_2,$$

small needles, is characterised by its sparing solubility in water, 100 c.c. of which dissolves only 0·2372 gram at the laboratory temperature (the *barium dipotassium* salt is practically insoluble in water). It is readily converted into *potassium ethylenediamine*-NN′-*disulphonate*, rectangular platelets, from which the corresponding free *acid*, shining leaflets, is obtained by means of perchloric acid, and, further, into ethylenediamine sulphate, the yield of the latter being 83% of that theoretically possible. H. W.

A New Method for Producing Hexamethylenetetramine. TH. SABALITSCHKA (*Zeitsch. angew. Chem.*, 1920, **33**, 217).—The formation of hexamethylenetetramine occurs, not only by the interaction of formaldehyde and free ammonia or ammonium carbonate, but also when a neutral ammonium salt, such as ammonium chloride, is employed in the absence of any alkali whatever. The quantitative aspect of the reaction in this case has not yet been investigated. G. F. M.

The Preparation of α-Derivatives of Hydroxylamine by means of Potassium Hydroxylaminedisulphonate. α-Methylhydroxylamine and αα-Ethylenedihydroxylamine. WILHELM TRAUBE, HEINRICH OHLENDORF, and HERBERT ZANDER (*Ber.*, 1920, **53**, [*B*], 1477—1492).—*Potassium α-methylhydroxylamine-ββ-disulphonate*, $OMe{\cdot}N(SO_3K)_2$, is readily obtained by shaking an aqueous solution of potassium hydroxylaminedisulphonate in the presence of that quantity of potassium hydroxide which is required to form the basic salt, $OK{\cdot}N(SO_3K)_2$, with methyl iodide, or, more rapidly, with methyl sulphate (the corresponding *lead*, *barium*, and *silver* salts are freely soluble in water), and is converted by being heated for a moment with dilute sulphuric acid into *α-methylhydroxylamine-β-sulphonic acid*, hygroscopic syrup, which is most readily isolated in the form of its *potassium* salt, well-formed, pearly plates (the *barium* salt, long, transparent prisms, $+1H_2O$, was analysed; the *lead* and *silver* salts are freely soluble in water). Protracted action of boiling sulphuric or hydrochloric acid on potassium methylhydroxylaminedisulphonate causes the elimination of both sulphonic groups and the formation of *α-methylhydroxylamine*, which is most readily isolated by adding an excess of alkali to the product of the action and distillation of the mixture with steam; the free base, b. p. 49—50°, is a colourless, mobile liquid with an amine-like odour. It reduces ammoniacal silver solution, but not Fehling's solution, at the ordinary temperature. The normal *sulphate*, m. p. 144°, the *nitrate*, large, transparent prisms, which detonate violently at

about 300°, and the *picrate*, m. p. 175°, are described. The base reacts with benzaldehyde to yield anti-*benzaldoxime* O-*methyl ether*, b. p. 191°, and with alloxan to give *methyl violurate*, m. p. 258—265°; it is converted by an aqueous solution of potassium cyanate into *methoxycarbamide*, m. p. 82—83°, by phenylthiocarbimide into N-*phenyl*-N′-*methoxythiocarbamide*, m. p. 116°, and by ethyl chloroformate into methoxyurethane, colourless oil, b. p. 186—188°. It combines with carbon disulphide to yield the very unstable *salt*, $OMe\cdot NH_2,HS\cdot CS\cdot NH\cdot OMe$, which was analysed in the form of the corresponding *silver* compound, $C_2H_3ONS_2Ag_2$, intensely yellow precipitate, which decomposes above 40°.

Potassium ethylhydroxylaminedisulphonate, well-formed clusters of needles, is considerably more slowly formed from basic potassium hydroxylaminedisulphonate than is the corresponding methyl derivative, and is converted successively into *potassium ethylhydroxylaminemonosulphonate*, shining needles, readily soluble in water (the *free acid* is hygroscopic), and ethylhydroxylamine hydrochloride, m. p. 126°. Epichlorohydrin and the basic sulphonate yield *potassium epihydrinhydroxylaminedisulphonate*,

$\begin{matrix} O— \\ CH_2 \end{matrix}\!>CH\cdot CH_2\cdot O\cdot N(SO_3K)_2$, six-sided platelets. Similarly, ethylene dibromide gives *potassium αα′-ethylenedihydroxylaminetetrasulphonate*, $C_2H_4[O\cdot N(SO_3K)_2]_2$; the corresponding *silver* and *lead* salts are freely soluble in water, but a mixed *potassium barium* salt dissolves more sparingly. The tetrasulphonate is transformed successively into the very soluble *potassium αα′-ethylenedihydroxylaminedisulphonate* and into *αα′-ethylenedihydroxylamine*,

$$NH_2\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot NH_2,$$

colourless liquid with a faint odour, b. p. 203°/atmospheric pressure (frequently accompanied by violent explosion), 105°/23 mm. It is only feebly alkaline in aqueous solution. The following derivatives are described: *sulphate*, m. p. 260°, which has an acid reaction in aqueous solution; *hydrochloride*, m. p. 233°; *nitrate*, m. p. 124°, which detonates when heated above its melting point; *biscarbamide*, $C_2H_4(O\cdot NH\cdot CO\cdot NH_2)_2$, colourless crystals, m. p. 190°; *bisphenylthiocarbamide*,

$$C_2H_4(O\cdot NH\cdot CS\cdot NHPh)_2,$$

m. p. 119°.

Basic potassium hydroxylaminedisulphonate reacts comparatively rapidly with benzenesulphonyl chloride, *potassium benzenesulphohydroxylaminedisulphonate*, $SO_2Ph\cdot O\cdot N(SO_3K)_2$, needles, moderately soluble in water being formed.

The action of cyanogen bromide or iodide on basic potassium hydroxylaminedisulphonate results in the formation of *potassium iminocarbonyldihydroxylaminetetrasulphonate*,

$$NH{:}C[O\cdot N(SO_3K)_2]_2,$$

small needles ($+2H_2O$); this salt is invariably produced when one molecular proportion of the cyanogen haloid is mixed with one or two molecular proportions of the salt, and appears to be formed by the condensation of a molecule of potassium cyanohydroxyl-

aminedisulphonate primarily produced with a further molecule of the basic salt. H. W.

Action of Diazomethane on Amino-acids. J. HERZIG and KARL LANDSTEINER (*Biochem. Zeitsch.*, 1920, **105**, 111—114).—The results of further experiments by Schuster (compare A., 1914, i, 753) show that Geake and Nierenstein's supposed proof of the betaine structure of the amino-acids (A., 1914, i, 1057) cannot be accepted as of general validity.

When glycine is treated with diazomethane, most of the former remains undissolved, the methoxyl value of the dissolved part being almost zero, and estimation of methylimide group giving a value only slightly above that obtained with glycine alone. Hippuric acid is converted mostly into the methyl ester. With alanine, which mostly remains undissolved, the soluble part contains 3·79% of methoxyl group. Phenylalanine and diazomethane yield an oil of the composition $CH_2Ph\cdot CH(NHMe)\cdot CO_2Me$. These results and those obtained with leucine, glutamic acid, and tyrosine show that with only the two lowest amino-acids, glycine and alanine, diazomethane effects virtually no substitution, and that in either case introduction of a negative group into the molecule enhances the reactivity towards diazomethane. With the other amino-acids examined, a distinction must be made between substitution of the hydrogen of the carboxyl and amino-groups; substitution is almost complete in the former group, and takes place only with difficulty in the latter. The presence of free amino-acid is rendered probable by the reactivity of the carboxyl group, entry of the methyl residue at the nitrogen being possibly hindered by other unknown factors. According to Geake and Nierenstein's view, that absence of reactivity towards diazomethane in ethereal suspension constitutes a proof of the betaine structure of an amino-acid, such structure can be ascribed only to glycine and possibly to alanine, equilibrium between the betaine form and the ordinary form being assumed in other cases. The accuracy of Geake and Nierenstein's view is supported by the behaviour of glutamic acid. T. H. P.

Syntheses of β-Amino-acids from Substituted Ammonium Malonates and Formaldehyde. C. MANNICH and B. KATHER (*Ber.*, 1920, **53**, [*B*], 1368—1371).—The action of formaldehyde on aqueous solutions of the salts of malonic acid and amines leads to the formation of β-amino-acids, in accordance with the equation

$$CO_2H\cdot CHR\cdot CO_2H + NR_2'H + CH_2(OH)_2 = CO_2H\cdot CR(CH_2\cdot NR_2')\cdot CO_2H + 2H_2O.$$

The reaction is most successfully applied to monoalkylmalonic acids and secondary amines, since, in this case, each component only contains one replaceable hydrogen atom, and action can only proceed in one direction. Malonic acid contains two and ammonia three hydrogen atoms, all of which can react with formaldehyde, so that the product of the change is too complex to permit the isola-

tion of individual substances. In the condensation, the nitrogen atom invariably occupies the β-position to the carboxyl group. The action of heat on the β-aminodibasic acid results, in general, in the loss of carbon dioxide and amine, and the formation of an unsaturated acid.

ω-Dimethylaminodimethylmalonic acid,

$$CO_2H\cdot CMe(CH_2\cdot NMe_2)\cdot CO_2H,$$

from methylmalonic acid, dimethylamine, and formaldehyde, forms small prisms, m. p. about 98° (decomp.), and is decomposed by heat into carbon dioxide, dimethylamine, and methylacrylic acid. *Methyliminobisdimethylmalonic acid*,

$$(CO_2H)_2CMe\cdot CH_2\cdot NMe\cdot CH_2\cdot CMe(CO_2H)_2,$$

decomposes, with evolution of gas, at 83—84°, and cannot be preserved indefinitely at the ordinary temperature; it yields methylacrylic acid when heated. *ββ'-Tetramethyldiamino*iso*butyric acid* (from malonic acid, dimethylamine, and formaldehyde), needles, m. p. 139°, forms a *dihydrochloride*, slender needles, m. p. 169°, which gives a sparingly soluble double salt with mercuric chloride. Formaldehyde and methylammonium malonate yield a complex mixture, from which an *aurichloride*, $C_5H_{10}O_2NAuCl_4$, was isolated with difficulty. H. W.

The Preparation of Guanidine by the Interaction of Dicyanodiamide and Ammonium Thiocyanate. EMIL ALPHONSE WERNER and JAMES BELL (T., 1920, **117**, 1133—1136).

Fixation of Labile, Hydrated Forms by means of Mercuric Cyanide. G. SCAGLIARINI and E. BONINI (*Gazzetta*, 1920, **50**, ii, 114—117).—Treatment of cobalt or nickel sulphate solution with mercuric cyanide solution yields the isomorphous double sulphates, $CoSO_4,Hg(CN)_2,10H_2O$ and $NiSO_4,Hg(CN)_2,10H_2O$, the former orange-red and the latter greenish-blue. By similar procedure the salts, $Co(NO_3)_2,Hg(CN)_2,6H_2O$ and $Ni(NO_3)_2,Hg(CN)_2,6H_2O$, may be obtained. When the complex cobalt sulphate is electrolysed in aqueous solution, the mercuric cyanide migrates to the cathode, and must hence be united, partly at least, to the cobalt atom (compare Kurnakov, A., 1898, ii, 475; Barbieri and Calzolari, A., 1911, i, 184, 266, 268). T. H. P.

Mercury Derivatives of Ethylene. W. MANCHOT and ARTHUR KLÜG (*Annalen*, 1920, **420**, 170—190).—The mercuration of ethylene has been described by Hofmann and Sand in a series of communications during the years 1900 and 1901, as the final result of which they are led to consider that two types of substances are produced, to which they assign the formulæ $OH\cdot CH_2\cdot CH_2\cdot HgX$ and $X\cdot Hg\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot HgX$ respectively. It has been shown, however, that the mercurated derivatives of acetylene are to be regarded as true acetylene derivatives (Manchot and Haas, A., 1913, i, 1009; Manchot and Mährlein, A., 1919, i, 145), and arguments are now advanced in favour of regarding the ethylenic compounds as additive substances, $C_2H_4,HgX\cdot OH$ and $2C_2H_4,O(HgX)_2$.

Hofmann and Sand's formula does not readily explain why their

compound is immediately decomposed by halogen acids with the violent evolution of acetylene, whereas it is stable towards other acids. According to the authors' experiments, a similar result is produced by the addition of potassium cyanide or potassium thiocyanate in the presence of acid. In general, the reaction is caused by all those substances which combine with mercuric haloids to yield additive compounds of the type $HgCl_2,2HCl$, and may be expressed by the equations: $C_2H_4,OH{\cdot}HgCl + HCl \rightleftharpoons C_2H_4,HgCl_2 + H_2O$ and $C_2H_4,HgCl_2 + 2HCl \rightleftharpoons HgCl_2,2HCl + C_2H_4$. In support of this hypothesis, it is shown that compounds of the type $HgX_2,2HX$ can be isolated, although with some difficulty, and that the most characteristic substance of this class is $Hg(SCN)_2,2HSCN$, and further that aqueous solutions of mercuric chloride readily absorb ethylene with ultimate disappearance of the ionic reactions of mercury, and that the absorption is very much less marked when hydrochloric acid is added to the mercuric chloride solution. Further, as is to be expected from the equation $C_2H_4,OH{\cdot}HgCl + NaCl \rightleftharpoons C_2H_4,HgCl_2 + NaOH$, decomposition of the additive compound can be effected by the addition of alkali haloids, but, in consequence of the back action, the effect is not very marked, and is most noticeable when potassium thiocyanate is employed.

It has been observed previously by Sand that the complex, $C_2H_4,Hg(OH){\cdot}$, behaves as a univalent radicle, and, in this connexion, the *dichromate*, $[C_2H_4,Hg(OH)]_2Cr_2O_7$, has now been prepared. The free *base*, $[C_2H_4,Hg(OH)]{\cdot}OH$, has also been isolated by the action of moist silver oxide on the corresponding bromide as a viscous mass which freely evolves ethylene on treatment with hydrochloric acid (the *platinichloride*, $[C_2H_4,Hg(OH)]_2PtCl_6,5H_2O$, was analysed). Contrary to the statement of Sand, the benzoyl derivative, $C_2H_4,Hg(OBz)I$, evolves ethylene when treated with hydrochloric acid, the comparative slowness of the action being due to the insolubility of the substance.

The decomposition of mercurated ethylene compounds by iodine is readily explained by the additive formula; the primary action consists in the displacement of oxygen by iodine (which is in accordance with the well-known properties of mercury salts), followed by addition of oxygen at the double bond, thus yielding $CH_2I{\cdot}CH_2{\cdot}OH$ and $O(CH_2{\cdot}CH_2I)_2$ respectively. The action of alkyl iodide lends further support to the additive hypothesis; according to Sand's formulation, the ethanol derivative, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}HgI$ should yield propyl alcohol when treated with methyl iodide, whereas it actually gives methyl alcohol, ethylene, and mercuric iodide. Similarly, the ethyl ether mercuri-salts yield ethylene in abundance when heated with methyl iodide at 110°, $2C_2H_4,HgI{\cdot}O{\cdot}HgI + 2CH_3I = 2C_2H_4 + 2HgI_2 + (CH_3)_2O$. H. W.

Relations between the Constitution and Physical Properties of Hydroaromatic Compounds. K. von Auwers (*Annalen*, 1920, **420**, 84—111. Compare A., 1916, i, 130—131).—The present communication is mainly devoted to the *cyclo*hexanes.

Since it is quite possible that stereoisomeric forms of these may be obtained according to the method of operation, they have in general been prepared according to a uniform scheme which starts from the requisite *cyclo*hexanol obtained by Sabatier's method. The secondary *cyclo*hexanols are converted into the iodides, and these are reduced to the hydrocarbons in accordance with Zelinski's method. The process is not readily applicable to tertiary *cyclo*hexanols, since unsaturated hydrocarbons are readily produced; in these cases it is preferable first to transform them by phosphorus pentachloride into the chloro-compounds and to reduce the latter by sodium in the presence of moist ether, the latter operation being performed as slowly as possible. The products invariably contain small amounts of unsaturated hydrocarbons, which are removed by the addition of a slight excess of bromine followed by distillation in a vacuum. The products are ultimately distilled over sodium, and must finally neither show Beilstein's halogen test nor be coloured by tetranitromethane.

The validity of the rules governing the relation between constitution and physical properties which were propounded previously (*loc. cit.*) has been confirmed for a series of compounds, and certain apparent exceptions have been removed. Experiments directed to explain these exceptions have shown that the hydrogenation of benzene derivatives may lead to the formation of different stereoisomeric forms of the corresponding hydroaromatic derivatives when different methods are employed, and that with simple derivatives of *cyclo*hexane the physical constants of stereoisomeric modifications may differ considerably.

The following compounds are described: 1:2-Dimethyl*cyclo*hexan-2-ol, b. p. 169°/ordinary pressure, 63—65°/9 mm., $D_4^{13\cdot7}$ 0·9252, D_4^{20} 0·920, $n_\alpha^{13\cdot7}$ 1·46035, $n_D^{13\cdot7}$ 1·46248, $n_\beta^{13\cdot7}$ 1·46848, $n_\gamma^{13\cdot7}$ 1·47330, n_D^{20} 1·4596; 2-*chloro*-1:2-*dimethyl*cyclo*hexane*, colourless oil, b. p. 53—54°/9 mm., $D_4^{13\cdot3}$ 0·9708, D_4^{20} 0·965, $n_\alpha^{13\cdot3}$ 1·46492, $n_D^{13\cdot3}$ 1·46723, $n_\beta^{13\cdot3}$ 1·47407, n_D^{20} 1·4642; 1:2-dimethyl*cyclo*hexane, b. p. 35—37°/23 mm., 122·5—123·5°/760 mm. (?), $D_4^{17\cdot85}$ 0·7809, D_4^{20} 0·779, $n_\alpha^{17\cdot85}$ 1·42820, $n_D^{17\cdot85}$ 1·43020, $n_\beta^{17\cdot85}$ 1·43592, $n_\gamma^{17\cdot85}$ 1·44056, n_D^{20} 1·4292; 4-*chloro*-1:4-*dimethyl*cyclo*hexane*, b. p 50·5—52°/14 mm., $D_4^{18\cdot5}$ 0·9438, D_4^{20} 0·943, $n_\alpha^{18\cdot5}$ 1·45088, $n_D^{18\cdot5}$ 1·45372, $n_\beta^{18\cdot5}$ 1·45942, $n_\gamma^{18\cdot5}$ 1·46462, n_D^{20} 1·4530; 1:4-dimethyl*cyclo*hexane, b. p. 119·5—120·5°, $D_4^{15\cdot7}$ 0·7722, D_4^{20} 0·769, $n_\alpha^{15\cdot7}$ 1·42407, $n_D^{15\cdot7}$ 1·42597, $n_\beta^{15\cdot7}$ 1·43174, $n_\gamma^{15\cdot7}$ 1·43624, n_D^{20} 1·4240; 1:2-dimethyl*cyclo*hexan-4-ol, b. p. 188—188·5°, $D_4^{12\cdot5}$ 0·9118, D_4^{20} 0·906, $n_\alpha^{12\cdot5}$ 1·45826, $n_D^{12\cdot5}$ 1·46012, $n_\beta^{12\cdot5}$ 1·46645, $n_\gamma^{12\cdot5}$ 1·47121, n_D^{20} 1·4570; 1:4-*dimethyl*cyclo*hexan-4-one*, mobile oil, b. p. 187°, $D_4^{12\cdot6}$ 0·9121, D_4^{20} 0·906, $n_\alpha^{12\cdot6}$ 1·44871, $n_D^{12\cdot6}$ 1·45094, $n_\beta^{12\cdot6}$ 1·45712, $n_\gamma^{12\cdot6}$ 1·46208, n_D^{20} 1·4476 (a second specimen purified through the *semicarbazone*, needles, m. p. 189°, had $D_4^{12\cdot5}$ 0·9116, D_4^{20} 0·906, $n_\alpha^{12\cdot5}$ 1·44856, $n_D^{12\cdot5}$ 1·45068, $n_\beta^{12\cdot5}$ 1·45692, $n_\gamma^{12\cdot5}$ 1·46188, n_D^{20} 1·4473); a mixture of 1:2-*dimethyl*-Δ^3- and -Δ^4-cyclo*hexenes*, obtained by the action of anhydrous oxalic acid on 1:2-dimethyl*cyclo*hexan-4-ol, b. p. 123·5—124·5°, D_4^{20} 0·8059, n_α^{20} 1·44290, n_D^{20} 1·44529, n_β^{20} 1·45205, n_γ^{20} 1·45757; 5-*chloro*-1:3:5-*trimethyl*cyclo*hexane*, b. p. 53—53·5°/10 mm., $D_4^{13\cdot7}$ 0·9344 ($D_4^{13\cdot9}$ 0·9342)

D_4^{20} 0·929, $n_\alpha^{13\cdot9}$ 1·45566, $n_D^{13\cdot9}$ 1·45775, $n_\beta^{13\cdot9}$ 1·46412, $n_\gamma^{13\cdot9}$ 1·46925, n_D^{20} 1·4550; 1 : 3 : 5-trimethyl*cyclo*hexane, b. p. 137·5°, $D_4^{13\cdot1}$ 0·7777, D_4^{20} 0·772, $n_\alpha^{13\cdot1}$ 1·42971, $n_D^{13\cdot1}$ 1·43175, $n_\beta^{13\cdot1}$ 1·43764, $n_\gamma^{13\cdot1}$ 1·44235, n_D^{20} 1·4286; 1 : 2 : 5-*trimethyl*cyclo*hexan*-4-*ol*, viscous oil, b. p. 195—197°/760 mm. (?), 79—79·6°/10 mm., $D_4^{19\cdot2}$ 0·8988, D_4^{20} 0·898, $n_\alpha^{19\cdot2}$ 1·45639, $n_D^{19\cdot2}$ 1·45851, $n_\beta^{19\cdot2}$ 1·46459, $n_\gamma^{19\cdot2}$ 1·46938, n_D^{20} 1·4582; 1 : 2 : 5-*trimethyl*cyclo*hexan*-4-*one*, mobile oil, b. p. 195—196°, $D_4^{17\cdot4}$ 0·8989, D_4^{20} 0·897, $n_\alpha^{17\cdot4}$ 1·44797, $n_D^{17\cdot4}$ 1·45010, $n_\beta^{17\cdot4}$ 1·45618, $n_\gamma^{17\cdot4}$ 1·46112, n_D^{20} 1·4489 (a second preparation, purified through the *semicarbazone*, small needles, m. p. 175·5—176·5°, had b. p. 194—195°, $D_4^{14\cdot35}$ 0·8998, D_4^{20} 0·895, $n_\alpha^{14\cdot35}$ 1·44827, $n_D^{14\cdot35}$ 1·45039, $n_\beta^{14\cdot35}$ 1·45647, $n_\gamma^{14\cdot35}$ 1·46140, n_D^{20} 1·4479); 1 : 2 : 5-trimethyl*cyclo*hexane, b. p. 44—45°/12 mm., 140—141°/760 mm. (?), $D_4^{16\cdot9}$ 0·7799, D_4^{20} 0·778, $n_\alpha^{16\cdot9}$ 1·42860, $n_D^{16\cdot9}$ 1·43056, $n_\beta^{16\cdot9}$ 1·43632, $n_\gamma^{16\cdot9}$ 1·44099, n_D^{20} 1·4292; 1 : 2 : 5-*trimethyl*-Δ^4-cyclo*hexene*, obtained by the action of phosphoric oxide on 1 : 2 : 5-trimethyl*cyclo*hexan-4-ol and possibly containing a small proportion of 1 : 2 : 5-trimethyl-Δ^3-*cyclo*hexene, b. p. 144—146°, $D_4^{16\cdot15}$ 0·8078, D_4^{20} 0·805, $n_\alpha^{16\cdot15}$ 1·44742, $n_D^{16\cdot15}$ 1·44990, $n_\beta^{16\cdot15}$ 1·45683, $n_\gamma^{16\cdot15}$ 1·46264, n_D^{20} 1·4482; 1 : 2 : 4 : 5-*tetramethyl*cyclo*hexan*-4-*ol*, b. p. 83·2—86·8°/13 mm., 195—196°/760 mm. (?), $D_4^{16\cdot5}$ 0·8997, D_4^{20} 0·897, $n_\alpha^{16\cdot5}$ 1·45782, $n_D^{16\cdot5}$ 1·45999, $n_\beta^{16\cdot5}$ 1·46608, $n_\gamma^{16\cdot5}$ 1·47094, n_D^{20} 1·4584; 4-*chloro*-1 : 2 : 4 : 5-*tetramethyl*cyclo*hexane*, colourless oil, b. p. 69—71°/10 mm., $D_4^{13\cdot95}$ 0·9406, D_4^{20} 0·936, $n_\alpha^{13\cdot95}$ 1·46288, $n_D^{13\cdot95}$ 1·46515, $n_\beta^{13\cdot95}$ 1·47150, $n_\gamma^{13\cdot95}$ 1·47655, n_D^{20} 1·4624; 1 : 2 : 4 : 5-*tetramethyl*cyclo*hexane*, b. p. 160·5—161·5°, $D_4^{13\cdot1}$ 0·7910, D_4^{20} 0·785, $n_\alpha^{13\cdot1}$ 1·43517, $n_D^{13\cdot1}$ 1·43718, $n_\beta^{13\cdot1}$ 1·44307, $n_\gamma^{13\cdot1}$ 1·44772, n_D^{20} 1·4341; 1 : 2 : 4 : 5-*tetramethyl*-Δ^4-cyclo*hexene*, colourless oil, b. p. 165—167°, $D_4^{16\cdot5}$ 0·8199, D_4^{20} 0·817, $n_\alpha^{16\cdot5}$ 1·45617, $n_D^{16\cdot5}$ 1·45880, $n_\beta^{16\cdot5}$ 1·46597, $n_\gamma^{16\cdot5}$ 1·47192, n_D^{20} 1·4572; 1 : 1 : 3-trimethyl*cyclo*hexane, b. p. 137—138°, D_4^{25} 0·7868 ($D_4^{25\cdot3}$ 0·7866), D_4^{20} 0·790, $n_\alpha^{25\cdot3}$ 1·43177, $n_D^{25\cdot3}$ 1·43385, $n_\beta^{25\cdot3}$ 1·43998, $n_\gamma^{25\cdot3}$ 1·44453, n_D^{20} 1·4362; 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexen-4-one, b. p. 194—196°, $D_4^{16\cdot3}$ 0·9332, D_4^{20} 0·930, $n_\alpha^{16\cdot3}$ 1·47622, $n_D^{16\cdot3}$ 1·47951, $n_\beta^{16\cdot3}$ 1·48857, $n_\gamma^{16\cdot3}$ 1·49645, n_D^{20} 1·4779; 1 : 1 : 3-trimethyl*cyclo*hexan-4-one, b. p. 190—191°, $D_4^{16\cdot45}$ 0·9045, D_4^{20} 0·902, $n_\alpha^{16\cdot45}$ 1·44907, $n_D^{16\cdot45}$ 1·45130, $n_\beta^{16\cdot45}$ 1·45732, $n_\gamma^{16\cdot45}$ 1·46240, n_D^{20} 1·4497.

H. W.

Action of Chlorine on 3 : 5-Dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene. LEONARD ERIC HINKEL (T., 1920, **117**, 1296—1303).

Process for the Reduction of Aromatic Nitro-compounds. JOSEPH TCHERNIAC and SAMUEL HENRY DAVIES (Brit. Pat. 150412).—Aromatic nitro-compounds, particularly hydroxynitro-compounds, are reduced by treatment with a mixture of hydriodic and hydrochloric acids. The consumption of iodine may be reduced to a minimum by adding a substance, such as phosphorus, which in presence of water reconverts the liberated iodine into hydriodic acid. In these circumstances it is obviously immaterial whether iodine or hydriodic acid is used in the first instance. For example, *p*-nitrophenol (139 parts) is reduced by boiling under a reflux condenser with 36 parts of amorphous phosphorus, 13·9 parts of

iodine, and 180 parts of 20% hydrochloric acid, until the vapour of iodine appears in the condenser. G. F. M.

The Synthesis of some Nitro-derivatives of Toluene. OSCAR LISLE BRADY and PERCY NOEL WILLIAMS (T., 1920, **117**, 1137—1140).

Binary Equilibria of certain Nitro-derivatives of Toluene. M. GIUA (*Gazzetta*, 1920, **50**, ii, 101—113).—Bell and Herty (this vol., i, 152) contradict the author's conclusion that molecular compounds are formed in the three binary systems, *p*-nitrotoluene-2:4:6-trinitrotoluene, *p*-nitrotoluene–2:4-dinitrotoluene, and 2:4-dinitrotoluene–2:4:6-trinitrotoluene (A., 1914, i, 817). The author refutes this contradiction, and gives further evidence in support of his conclusions. The experimental data obtained by Wogrinz and Vári (this vol., i, 307) also support the author's case. T. H. P.

Solubility and Crystallisation of Trinitro-*m*-xylene in Different Solvents. LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], **2**, 278—284).—The following quantities of trinitro-*m*-xylene are dissolved per 100 c.c. of solvent:—Ethyl alcohol at 15°, 0·09 gram; at 78°, 0·65 gram. Amyl alcohol at 15°, 0·14 gram; at 128°, 10·3 grams. Acetone at 15°, 0·95 gram; at 57°, 4·27 grams. Ethyl acetate at 15°, 0·77 gram; at 76°, 5·43 grams. Glacial acetic acid at 15°, 0·4 gram; at 115°, 15·03 grams. Nitric acid (D 1·500) at 15°, 5·51 grams; at 90°, 51·1 grams. Benzene at 15°, 0·92 gram; at 80°, 10·0 grams. Chlorobenzene at 15°, 1·06 grams; at 180°, 108·58 grams. Nitrobenzene at 15°, 2·56 grams; at 90°, 19·60 grams. Carbon tetrachloride at 15°, 0·08 gram; at 75°, 0·96 gram. Toluene at 15°, 1·11 grams; at 110°, 21·7 grams. *m*-Xylene at 15°, 0·83 gram; at 90°, 9·25 grams. The crystals obtained from these solutions are in the form of needles, m. p. 180·5—182·5°. The solubility in aniline at 15° is 3·87 grams per 100 c.c.; boiling aniline reacts with trinitro-*m*-xylene, yielding substances which have not yet been investigated. W. P. S.

***p*-Toluenesulphonyl Derivatives of Amino-acids.** TAKESABURO OSEKI (*J. Tokyo Chem. Soc.*, 1920, **41**, 8—19).—The following *p*-toluenesulphonyl derivatives have been prepared by shaking a solution of the amino-acid in the equivalent amount of alkali with an ethereal solution of *p*-toluenesulphonyl chloride for two hours, sodium hydroxide being frequently added to neutralise the hydrochloric acid formed in the reaction; the products are recrystallised after treatment with hydrochloric acid: of glycine, needles, m. p. 146°; of alanine, needles, m. p. 92—94°; of valine, m. p. 110—111°; of leucine, needles, m. p. 111·5°; of phenylalanine, needles, m. p. 134—135°; of cystine, octahedra, m. p. 204—205°; of asparagine, m. p. 126—128°; of tyrosine, columns, m. p. 224—226° (this derivative does not give the Millon reaction, and

is insoluble in alkalis; by treatment with excess of hydrochloric acid it is converted into the derivative

$$C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot SO_2\cdot C_6H_4Me,$$

m. p. 117—119°); of tryptophan, needles, m. p. 176°; and of lysine and arginine, oils. CHEMICAL ABSTRACTS.

Mixed Crystals of 4 : 4′-Dichlorodiphenyl, 4 : 4′-Dibromodiphenyl, and 4 : 4′-Dimethyldiphenyl. K. MIELEITNER (*Zeitsch. Kryst. Min.*, 1920, **55**, 631—634).—Solutions in acetone of two of the compounds in variable proportions yielded measurable crystals with only a very limited range of miscibility in the case of the dichloro- and dibromo-compounds. The axial ratios (tabulated below) of the mixed crystals do not always lie between those of the corresponding pure compounds. An intimate interpenetration, rather than true isomorphous mixing, is therefore suggested.

Dichloro-. Per cent.	Dibromo-. Per cent.	Dimethyl-. Per cent.	a-axis.	c-axis.	D.
100·00	—	—	1·1569	0·7078	1·439
—	100·00	—	1·1181	0·6963	1·897
—	—	100·00	1·1722	0·7137	1·102
53·06	46·94	—	1·1278	0·6979	1·654
55·89	44·11	—	1·1316	0·6993	1·695
44·66	—	55·34	1·1504	0·7016	1·228
10·45	—	89·55	1·1802	0·7388	1·127
61·46	—	38·54	1·1571	0·7068	1·278
—	59·75	40·25	1·1416	0·6884	1·422

L. J. S.

Action of Amines on Trinitrophenylmethylnitroamine. THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and ROBERT ILLTYD LEWIS (T., 1920, **117**, 1273—1280).

New Syntheses of Hordenine. ERNST SPÄTH and PHILLIP SOBEL (*Monatsh.*, 1920, **41**, 77—90. Compare Barger, T., 1909, **105**, 2193; Rosenmund, A., 1910, i, 241; Léger, A., 1910, i, 336; Voswinckel, A., 1912, i, 443).—An ethereal solution of magnesium *p*-anisyl bromide is slowly added to dichlorodiethyl ether dissolved in ether at −15°, and the product, after being distilled under diminished pressure [b. p. 162—167°/16 mm. (decomp.)], is found to consist of a mixture of *β-chloro-α-p-methoxystyrlene*, $OMe\cdot C_6H_4\cdot CH:CHCl$, colourless liquid with an odour of aniseed, b. p. 137—140°/19 mm., and the desired *β-chloro-α-ethoxy-α-p-anisylethane*, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CH_2Cl$, the latter having partly lost ethyl alcohol during the process of distillation. The undistilled product of the reaction is, however, converted by anhydrous dimethylamine into *β-dimethylamino-α-ethoxy-α-anisylethane*, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CH_2\cdot NMe_2$, b. p. 152—153°/14 mm. (the *platinichloride* was analysed), which could not be satisfactorily converted into hordenine, since short treatment with hydriodic acid yielded a base which was not identical with hordenine, whilst pro-

longed action caused the elimination of nitrogen with the formation of non-basic products.

p-Methoxybenzyl bromide reacts with bromomethyl ether in dry ethereal solution to give a mixture of 4:4′-dimethoxydibenzyl and *β-methoxy-α-*p*-anisylethane*, $OMe\cdot C_6H_4\cdot CH\cdot CH_2\cdot OMe$, colourless liquid, b. p. 119—121°/12 mm. (the yield of the latter being 48% of that theoretically possible on the basis of the bromide used). Concentrated hydrobromic acid transforms the latter into *β-bromo-α-*p*-hydroxyphenylethane*, colourless, silky needles, m. p. 89—91°, b. p. 153—165°/14·5 mm. (some decomp.), which is converted by anhydrous dimethylamine at the ordinary temperature into hordenine, m. p. 117—118° in 82% yield.

β-Bromo-*p*-methoxystyrene reacts extremely slowly with an alcoholic solution of sodium acetate at 170°, but is converted by methyl alcoholic sodium methoxide at 160—170° into a mixture of *β-p-dimethoxystyrene*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot OMe$, b. p. 140—145°/16 mm., and *p*-anisylacetylene. The former is catalytically hydrogenated in the presence of palladised barium sulphate to *β*-methoxy-*α*-anisylethane, b. p. 121—123°/14 mm., which is converted into hordenine as described above, whilst the latter may be in part transformed into *β-p*-dimethoxystyrene by heating it with methyl alcoholic potassium hydroxide solution at 130—140°. H. W.

Tetranitromethane. II. Tetranitromethane as a Nitrating Agent. ERICH SCHMIDT and HEINRICH FISCHER (*Ber.*, 1920, **53**, [*B*], 1529—1537).—Decomposition of tetranitromethane into nitroform and nitric acid which has been shown previously (A., 1919, i, 248) to occur almost exclusively under the action of very concentrated aqueous alkali is found to take place in the presence of a weak base if solutions in alcohol or acetone are employed. This is shown to occur at the instances of dimethyl- and diethyl-*p*-toluidine, which thereby undergo nitration by the liberated nitric acid. The same effect can be obtained with suitable non-basic materials if the reaction is performed in the presence of pyridine (which thereby forms the nitroform salt). The process thus constitutes the first method of introducing the nitro-group into the aromatic nucleus in a non-acid medium.

*3-Nitrodimethyl-*p*-toluidine-nitroform*,

$$NMe_2\cdot C_6H_3Me\cdot NO_2,CH(NO_2)_3,$$

yellow crystals which slowly decompose when preserved at the ordinary temperature, and evolve gas at 91—92°, is prepared by the gradual addition of an alcoholic solution of tetranitromethane to an ice-cold solution of dimethyl-*p*-toluidine and boric acid in alcohol. (The analysis of this and similar compounds is effected by estimating the nitroform, since they do not give concordant results for carbon, hydrogen, and nitrogen by the usual method.) The constitution of the substance is elucidated by its reduction to 3-aminodimethyl-*p*-toluidine, b. p. 115—117°/12 mm., 69—71°/0·5 mm. (acetyl derivative, m. p. 111—112°), by its fusion by alkali into 3-nitrodimethyl-*p*-toluidine, b. p. 110—113°/0·5 mm., and

by its direct synthesis from its components in aqueous-alcoholic solution. 3-*Nitrodiethyl*-p-*toluidine-nitroform*, yellow crystals which decompose at 91°, is similarly converted into 3-*nitrodiethyl*-p-*toluidine*, b. p. 101—102°/0·2 mm. 3-*Nitrodimethyl*-p-*anisidine-nitroform*, yellow crystals which decompose at 108° after previous discoloration and can only be preserved for a few hours at the ordinary temperature, and 3-*nitrodimethyl*-p-*anisidine*, b. p. 108—110°/0·5 mm., are prepared in like manner.

The action of an alcoholic solution of tetranitromethane on *p*-cresol dissolved in an ice-cold mixture of alcohol and pyridine yields *m*-nitro-*p*-cresol, m. p. 33·5°, b. p. 73—75°/0·5 mm., in 60% yield, and *pyridine nitroform*, which decomposes at 91—92° and cannot be long preserved unchanged at the ordinary temperature.

[With ADALBERT WAGNER.]—A solution of *iso*safrole in acetone and pyridine is converted by tetranitromethane dissolved in acetone into β-nitro*iso*safrole, m. p. 98° (compare Wallach and Müller, A., 1904, i, 754), the yield being 72·5% of that theoretically possible.

[With WILLY BÄJEN.]—Anethole is similarly transformed into β-nitroanethole, m. p. 48°, in 64·3% yield. H. W.

Tetranitromethane. III. Conversion of Tertiary Amines into Secondary Nitrosoamines. I. ERICH SCHMIDT and HEINRICH FISCHER (*Ber.*, 1920, **53**, [*B*], 1537—1544).—When tetranitromethane is allowed to act on a boiling alcoholic solution of a tertiary base in the presence of pyridine, the nitrating action of the liberated nitric acid (compare preceding abstract) is only slightly evident, the main change consisting in the removal of an N-alkyl group as the corresponding aldehyde and the formation of a secondary nitrosoamine: $:N{\cdot}CH_2R + C_5H_5N + (NO_2)_2C\overset{\diagup O \diagdown}{\text{——}}N{\cdot}O{\cdot}NO_2 = :N{\cdot}NO + C_5H_5N,CH(NO_2)_3 + R{\cdot}CHO$. The action has so far been applied to fatty-aromatic amines, and does not appear to be influenced by the presence or position of further substituents in the ring. It is usually carried out in the following manner. An alcoholic solution of tetranitromethane (1·1 mol.) is slowly added to a boiling alcoholic solution of the tertiary amine (1 mol.) and pyridine (1·2—1·5 mol.), and ebullition is continued until the odour of tetranitromethane disappears. The mixture is poured into water and extracted with ether after addition of saturated salt solution. The ethereal solution is subjected to the action of steam in the presence of a further quantity of salt solution and a little potassium carbonate. Ether and the nitrosoamine are successively volatilised; the latter is freed from traces of pyridine by agitating its ethereal solution with dilute sulphuric acid, and subsequently purified in the usual manner. The following substances have been thus obtained: phenylmethylnitrosoamine, b. p. 86—87°/1·7 mm., and *p*-nitrophenylmethylnitrosoamine; phenylethylnitrosoamine, b. p. 96—97°/1·9 mm., and *p*-nitrophenylethylnitrosoamine; *o*-tolylmethylnitrosoamine, b. p. 89—90°/1·5 mm.; *o*-tolylethylnitrosoamine, b. p. 83—84°/0·6 mm.; *o*-chlorophenylmethylnitrosoamine, b. p. 89°/

1·2 mm.; *o*-anisylmethylnitrosoamine, b. p. 112°/1·1 mm., and *p*-nitro-*o*-anisylmethylnitrosoamine; m-*tolylmethylnitrosoamine*, orange-yellow oil, b. p. 89—90°/1 mm.; m-*chlorophenylmethylnitrosoamine*, nearly colourless leaflets, m. p. 36—37°; *p*-tolylmethylnitrosoamine, m. p. 52°, and 3-nitrodimethyl-*p*-toluidine; *p*-chlorophenylmethylnitrosoamine, m. p. 51°; p-*chlorophenylethylnitrosoamine*, colourless, interwoven needles, m. p. 60—61° (*p*-chlorodiethylaniline, which has been previously isolated by Hofmann in the crude condition, is obtained by the action of ethyl alcohol on *p*-chloroaniline hydrobromide at 150°, and forms colourless needles, m. p 30°, b. p. 95—96°/1·5 mm.); *m*:4-xylylmethylnitrosoamine, pale yellow oil, b. p. 101°/1·3 mm. H. W.

Halogenalkylated Aromatic Amines. V. Preparation of Aryl Vinyl Ethers. JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1920, **53**, [*B*], 1399—1408).—The preparation of vinyl ethers is generally a matter of considerable difficulty, and few members of this class are known. The authors have therefore investigated a possible general method of synthesis which depends on (1) the replacement of the halogen atom of β-halogenalkylated aromatic amines by the radicle OR; (2) union of the basic ethers thus produced with methyl iodide or methyl sulphate; and (3) decomposition of the quaternary salts so formed with alkali in accordance with the scheme $RO\cdot[CH_2]_2\cdot NR_3'\cdot I + KOH \rightarrow R\cdot O\cdot CH{:}CH_2 + NR_3$. Unfortunately, the process breaks down at the third stage, when R is an aliphatic residue, since the quaternary compounds are only decomposed with unusual difficulty, and are, in part, extensively changed and in part re-converted into the basic ether. With phenols, on the other hand, good results are obtained, and this is also the case with dihydroxy- and thio-phenols.

Peculiar interest attaches to the vinyl ethers from the point of view of the chemistry of perfumes, but the introduction of the vinyl complex is found to have a most irregular influence on the odour of the compounds produced.

N-β-*Naphthoxyethylmethylaniline*, $C_{10}H_7\cdot O\cdot[CH_2]_2\cdot NMePh$, m. p. 75°, b. p. 200—205°/mercury vacuum, is most readily prepared by heating β-naphthol with methylbromoethylaniline and potassium hydroxide in acetone solution. It is only feebly basic, but yields a *hydrochloride*, needles, m. p. 150°, a *platinichloride* decomposing at 128—129°, and a *methiodide*, m. p. 137°. Decomposition of the latter is best effected with boiling aqueous potassium hydroxide (15%), through which steam is blown continuously, whereby dimethylaniline and β-naphthyl vinyl ether are removed as soon as they are formed, whilst *N*-β-naphthoxyethylmethylaniline remains in the flask. The yield of the ether is 45—50% of that theoretically possible, whilst about a half of the original iodide is left as the corresponding base, which can be readily utilised for further preparations. β-*Naphthyl vinyl ether*, m. p. 63—64°, b. p. 137°/13 mm., has an intense odour of tangarine skins. In contrast to allyl ether (the same is true for all other representatives of this

class), it is not able to undergo the Claisen transformation into vinylated β-naphthol; the vinyl group does not unite with bromine smoothly, and is only very slowly and incompletely hydrogenated by Paal's method. The aromatic vinyl ethers are more stable towards hydrolysis than are the corresponding aliphatic compounds, and the odour of acetaldehyde is only apparent after protracted boiling with alkali hydroxide or dilute acid.

Carvacryloxyethylmethylaniline, $C_6H_3MePr\cdot O\cdot[CH_2]_2\cdot NMePh$, is a moderately viscous oil, b. p. 220—221°/11 mm., which yields a very soluble *picrate*, and an oily *hydrochloride* and *methiodide* (the *platinichloride* corresponding with the latter has m. p. 90°). *Carvacryl vinyl ether* has b. p. 217—218°/atmospheric pressure, and possesses an unpleasant odour dissimilar to that of the corresponding methyl or ethyl ether.

β-Tetrahydronaphthyloxyethylmethylaniline, b. p. 52—53°, b. p. 257—258°/14 mm., gives a *hydrochloride*, m. p. 163°, a *picrate*, m. p. 122°, and a *methiodide*, colourless, crystalline powder, m. p. 123°. *β-Tetrahydronaphthyl vinyl ether*, b. p. 121—122°/11 mm., has a faint, not unpleasant odour, which is less marked than that of the corresponding *allyl* ether, b. p. 158—161°/23 mm.

The action of methylbromoethylaniline on catechol leads to a mixture of o-*hydroxyphenoxyethylmethylaniline*, m. p. 71° (the *hydrochloride*, m. p. 195° after darkening above 140°, *picrate*, orange leaflets, m. p. 146°, *acetyl* derivative and *methiodide*, colourless leaflets, m. p. 135°, are described), and the symmetrical *bis-β-methylphenylaminoethyl ether of catechol*,

$$NMePh\cdot[CH_2]_2\cdot O\cdot C_6H_4\cdot O\cdot[CH_2]_2\cdot NMePh,$$

m. p. 90—91° (*hydrochloride*, *picrate*, yellow powder, m. p. 103°, *methiodide*, m. p. 96°). *Catechyl monovinyl ether*, b. p. 213°, is a colourless liquid with a faint odour. *Catechyl divinyl ether* has b. p. 206—209°.

Phenylthiolethylmethylaniline, $SPh\cdot[CH_2]_2\cdot NMePh$, almost odourless oil, b. p. 222—224°/14 mm. (*hydrochloride*, oily, *picrate*, yellow needles, m. p. 155°), yields an oily *methiodide* (the corresponding *platinichloride*, m. p. 155°, was analysed), which gives a 90% yield of *phenyl vinyl sulphide*, b. p. 200—201°, almost colourless liquid, which has a pleasant odour of radishes.

N-*Methyl-β-amyloxyethylaniline*, b. p. 154—156°/10 mm., is slowly formed in the usual manner; it yields oily salts and a non-crystalline *methiodide* (the corresponding *platinichloride* decomposes at 166° after darkening at 160°); when treated with potassium hydroxide, the quaternary iodide largely regenerates the original amine and only gives traces of a nitrogen-free oil with an ethereal odour.

N-*Methyl-β-thiocyanoethylaniline*, pale yellow oil, b. p. 186°/10 mm., is obtained with unusual ease from methyl-β-bromoethylaniline and potassium thiocyanate in aqueous-alcoholic solution, and yields a crystalline *methiodide*, m. p. 137—138°. The latter appears to be decomposed by potassium hydroxide primarily into dimethylaniline and *vinyl thiocyanate*; under the experimental conditions

adopted, however, the latter is unstable, and immediately decomposes in an undetermined direction. H. W.

Studies in Ring Formation. III. The Condensation of Aromatic Amines with α- and β-Diketones and with 4 : 4′-Diacetyldiphenyl. CLARENCE VICTOR FERRISS and EUSTACE EBENEZER TURNER (T., 1920, **117**, 1140—1151).

Influence of Substituents on Reactions. IV. Preferential Substitution Positions in β-Naphthylamine. HARTWIG FRANZEN and GUSTAV STÄUBLE (*J. pr. Chem.*, 1920, [ii], **101**, 58—74. Compare A., 1919, ii, 4).—It has been shown previously (Franzen and Aaslund, A., 1917, i, 644) that not more than three bromine atoms can be introduced readily into the β-naphthylamine molecule, forming successively 1-bromo-β-naphthylamine, 1 : 6-dibromo-β-naphthylamine (compare Claus and Philipson, A., 1891, 462), and a substance which has been considered by Claus and Jäck to be 1 : 4 : 6-tribromo-β-naphthylamine, but which is now shown to be the 1 : 3 : 6-derivative; this is deduced from the fact that the compound is converted by tin and hydrochloric acid into a dibromo-β-naphthylamine, which differs from the 1 : 6-derivative and after elimination of the amino-group yields 2 : 7-dibromonaphthalene. The authors are led to the conclusion that the positions 1, 6, and 3 are preferential substitution points in the bromination of β-naphthylamine; the β-amino-group has a much greater influence on the 1- than on the 6-hydrogen atom, whilst the latter is noticeably more influenced than the 3-hydrogen atom. The action of tin and hydrochloric acid on 1 : 6-dibromo-β-naphthylamine and 1 : 3 : 6-tribromo-β-naphthylamine leads essentially to the replacement of the 1-bromo-atom by hydrogen; in these two substances, the position 1 is a favoured substitution point with respect to hydrogen. In these cases also, therefore, the substituent in position 1 is much more influenced by the amino-group than that in position 3 or 6.

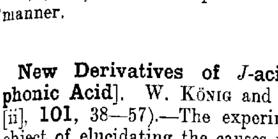
α-Bromonaphthalene is not reduced by tin and hydrochloric acid. 1-Bromo-β-naphthylamine is converted by tin and hydrochloric acid or by stannous chloride into β-naphthylamine, but is not affected by alcoholic potassium hydroxide solution. 1 : 6-Dibromo-β-naphthylamine is transformed by tin and hydrochloric acid, by stannous chloride, by hydriodic acid or by cuprous chloride and hydrochloric acid into 6-bromo-β-naphthylamine, m. p. 128° (the hydrochloride, *acetyl* derivative, m. p. 192°, and *benzoyl* derivative, colourless leaflets, m. p. 218°, are described). 6-Bromo-β-naphthylamine is scarcely affected by tin and hydrochloric acid or by hydriodic acid. 1 : 3 : 6-Tribromo-β-naphthylamine is reduced by tin and hydrochloric acid to 3 : 6-*dibromo-β-naphthylamine*, small, colourless leaflets, m. p. 187° (*acetyl* derivative, long, slender needles, m. p. 195°, *benzoyl* derivative, long, silky needles, m. p. 161—162°); a similar result is obtained by the use of stannous chloride. H. W.

The Preparation of Thiocarbimides from Non-Aromatic Primary Bases. JULIUS VON BRAUN (*Ber.*, 1920, **53**, [*B*], 1588).—Thiocarbimides of non-aromatic primary bases are most conveniently prepared by the thiuram disulphide method (van Braun and Deutsch, A., 1912, i, 673), which is particularly applicable to the production of fatty-aromatic, hydroaromatic, and complex thiocarbimides. *cyclo*Hexylthiocarbimide (compare Skita and Rolfis, this vol., i, 607) is obtained quantitatively from *cyclo*hexylamine in this manner.

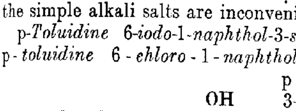
H. W.

New Derivatives of *J*-acid [6-Amino-1-naphthol-3-sulphonic Acid]. W. KÖNIG and H. HALLER (*J. pr. Chem.*, 1920, [ii], **101**, 38—57).—The experiments were undertaken with the object of elucidating the causes which condition the peculiar tinctorial properties of derivatives of *J*-acid as compared with those derived from similar acids. In most of the work which has been accomplished previously, the alterations have been effected by alkylating, arylating, etc., the amino-group. The present communication describes the production of compounds obtained by replacement of the amino- by other radicles and by altering the sulphonic acid group; the consideration of the tinctorial properties of the substances is reserved for a subsequent paper. The following individual substances are described, which are generally prepared by well-known methods. In the case of the sulphonic acids, the *p*-toluidine salts have been investigated, since the free acids and the simple alkali salts are inconveniently freely soluble in water.

p-*Toluidine* 6-*iodo*-1-*naphthol*-3-*sulphonate*, pale pink leaflets; p-*toluidine* 6-*chloro*-1-*naphthol*-3-*sulphonate*, grey leaflets; p-*toluidine* 6-*azido*-1-*naphthol*-3-*sulphonate*, shining, transparent, colourless leaflets (the *disodium* salt is also described); 6-*β*-*hydroxynaphthaquinonimido*-1-*naphthol*-3-*sulphonic acid* (annexed formula), violet powder;



6-*hydrazino*-1-*naphthol*-3-*sulphonic acid*, small, colourless needles; p-*toluidine* 6-*isatin*-1-*hydroxy*-2-*naphthylhydrazine*-3-*sulphonate*, lemon-yellow powder; 1(7′-*sulpho*-5′-*hydroxy*-2′-*naphthyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* (annexed formula), colourless needles by the action of ethyl acetoacetate on *p*-toluidine 6-azido-1-naphthol-3-sulphonate in the presence of alcoholic sodium ethoxide, followed by hydrolysis of the product with sodium hydroxide;



sodium 5 : 5′-*dibenzoyloxy*-2 : 2′ : 1 : 1′-*dinaphthacarbazole*-7 : 7′-*disulphonate*; *sodium* 6-*benzoylamino*-1-*benzoxynaphthalene*-3-*sulphonate*, small, silky needles; 6-*benzoylamino*-1-*benzoyloxynaphthalene*-3-*sulphonyl chloride*, yel-

low glassy mass, m. p. 151°; the corresponding *anilide*, colourless crystals, m. p. 155°; *6-benzoylamino-α-naphthol-3-sulphonanilide* (from the dibenzoyl compound and dilute sodium hydroxide solution), pale yellow powder, m. p. 125°, which readily couples with diazotised *p*-toluidine to yield a pale red, monoazo-dye; *phenyl-2-benzoylamino-5-hydroxy-7-naphthylsulphone* (from the corresponding acid chloride, benzene, and aluminium chloride), pale yellow powder, which blackens without melting when heated.

In connexion with the conversion of *J*-acid by bisulphite into "carbazole *J*-acid," the mechanism of Bucherer's reaction is fully discussed; the author is led to the conclusion that the primary products are sulphurous esters, but the original paper must be consulted for details. H. W.

Alkali Fusions. II. Fusion of Sodium Benzene-*m*-disulphonate with Sodium Hydroxide for the Production of Resorcinol. MAX PHILLIPS and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, **12**, 857—860).—The maximum yield of resorcinol is obtained by fusing 20 to 24 mols. of sodium hydroxide with 1 mol. of sodium benzene-*m*-disulphonate, but in practice the yields were nearly as good (60·1 to 63·5%) when only 16 mols. of alkali were used. The best temperature was 310°, and the time two hours. At 330—350° there was some destruction of resorcinol, whilst at 270—290° the yields were lower, owing to the reaction being incomplete, and even by extending the time of fusion were not so good as at 310°. The presence of water in the fusion mixture reduces the yield of resorcinol, but does not make a very material difference if it does not exceed 2 to 4%. C. A. M.

Tautomerism of Phenols. Resorcinol. HANS TH. BUCHERER (*Ber.*, 1920, **53**, [*B*], 1457—1459).—The action of sodium hydrogen sulphite on a boiling aqueous solution of resorcinol slowly leads to the formation of a substance, $C_6H_9O_{11}S_3Na_3$, which has been regarded by Fuchs and Elsner (this vol., i, 545) as the sodium salt of the bisulphite compound of *cyclo*hexane-3:5-dionesulphonic acid. The stability of this compound towards boiling dilute mineral acids causes the author to doubt the constitution assigned to it and to consider it as allied to the sulphurous esters of mono- and di-hydric phenols, which he has shown to be characterised in this manner. It is further pointed out that Bucherer and Schenkel (A., 1908, i, 452) have obtained a compound, $C_5H_5N,3NaHSO_3,2H_2O$, from pyridine and bisulphite in which the pyridine nucleus is extensively altered, since the greater part of the pyridine nitrogen is readily liberated in the form of ammonia by cold dilute alkali; it therefore appears that cyclic systems with two or three molecules of bisulphite can be obtained readily and without the necessity of intervention of carbonyl groups. H. W.

Tautomerism of Resorcinol. J. HERZIG and S. ZEISEL (*Ber.*, 1920, **53**, [*B*], 1518).—In connexion with the recent publication

on this subject by Fuchs and Elsner (this vol., i, 545), the authors point out that they have conclusively proved the possibility of tautomerism in this substance by the action of potassium hydroxide and alkyl iodide. H. W.

Syntheses of Humic Acids. WILHELM ELLER and KÄTE KOCH (*Ber.*, 1920, **53**, [*B*], 1469—1476).—The oxidation of phenols in alkaline solution leads to the formation of substances which appear to be identical in all respects with the natural humic acids; only such phenols, however, as are capable of giving quinonoid intermediate products show this behaviour. The acids are obtained by allowing the alkaline solutions of the phenol to remain exposed to the air, or, more rapidly, by the addition of finely powdered potassium persulphate to the solution. The products from catechol, quinol, and *p*-benzoquinone give analytical figures in agreement with the formula $C_6H_4O_3$, but since the acids do not crystallise and cannot be purified by repeated precipitation, the purity of the substances can only be controlled by analysis of several independently prepared specimens. The synthetic substances are soluble in water and alcohol, and, to some extent, in ether, but this property is lost when they become dry. In proportion as they are washed free from mineral acid, they develop the power of forming colloidal solutions in water. The moist substances shrink greatly when dried, and at 100° lose water, forming hard, brittle masses, which are readily ground to a black, shining powder. Their alkali salts dissolve readily, the remaining salts very sparingly, in water. In these respects they behave exactly as do the natural humic acids, and the similarity also extends to their behaviour towards chlorine, nitric acid, sodium hypobromite, and acetic anhydride.

The humic acid obtained from phenol resembles the other synthetic products, except in its greater solubility in alcohol; it has, however, been so far impossible to obtain concordant analytical data for the product.

The work is considered to throw considerable light on the chemistry of the natural humic acids, since it proves definitely that a number of them are existant, and that the pure substances are free from nitrogen and are possessed of definite acidic properties (probably owing to the presence of an unchanged phenolic hydroxyl group). They are probably formed by elimination of water from the hexoses, with formation of quinones, $C_6H_{12}O_6 = 4H_2O + C_6H_4O_2$, and subsequent oxidation of the latter to humins; an experimental realisation of the first step in this hypothetical scheme has not yet been accomplished satisfactorily. H. W.

Diphenylene Sulphide in Coal Tar. O. KRUBER (*Ber.*, 1920, **53**, [*B*], 1566—1567. Compare Weissgerber and Kruber, this vol., i, 754).—The presence of diphenylene sulphide in crude phenanthrene (containing about 1% of sulphur) is established by

oxidising the latter with hydrogen peroxide in acetic acid solution, whereby diphenylenesulphone, m. p. 229—230°, is obtained.

H. W.

Diphenylaryltelluronium Salts. KARL LEDERER (*Ber.*, 1920, **53**, [*B*], 1430—1445. Compare A., 1916, i, 810; 1917, i, 134).—The preparation of the diphenylaryltelluronium salts is effected by the addition of the requisite Grignard reagent (two or, more usually, three times the calculated quantity is used) to a solution of diphenyltelluronium dichloride in dry toluene. The mixture is shaken and immediately treated with dilute hydrochloric acid, after which any residual solid is dissolved in boiling water. The solution is treated with potassium iodide in quantity sufficient to convert the telluronium salt into the iodide, when the latter separates, whilst a further quantity may be obtained by treatment of the filtrates with sulphurous acid, and subsequent concentration. It is frequently contaminated with basic iodide, in which case it is again dissolved in water, the solution is treated with acetic acid and potassium iodide, and subjected to protracted boiling, whereby the basic iodide is decomposed, with the separation of the di-iodide, which can readily be separated by filtration. The following series are described.

Diphenyl-p-*tolyltelluronium Salts.*—*Iodide*, colourless, crystalline powder, m. p. 219—220°; *bromide*, colourless needles, m. p. 228—229° after softening at 226°; *chloride*, partly crystalline mass; *picrate*, monoclinic prisms, m. p. 132—133° after softening at 130°; *mercuri-iodide*, microscopic needles, m. p. 222—223° after softening at 220°; *mercurichloride*, resinous mass.

Diphenyl-o-*tolyltelluronium Salts.*—*Iodide*, small crystals, m. p. 175—176° after softening at about 170° (*mercuri-iodide*, white, amorphous powder, which softens from about 154° and is completely melted at 184°); *chloride*, a resin; *mercurichloride*, colourless needles, m. p. 210—211° after softening at 207—208°; *bromide*, microscopic prisms, m. p. about 203° after softening at about 199°; *picrate*, small, triclinic crystals, m. p. 127—128° after softening at 122°.

Diphenyl-m-*tolyltelluronium Salts.*—*Iodide*, colourless needles, m. p. 190—191° (from water), 202° after softening at 200° (from alcohol); *mercuri-iodide*, cubic crystals from alcohol, m. p. 134—135° after softening at 132°, slender needles from glacial acetic acid, m. p. 132—133° after softening at 129°; the *chloride* and *mercurichloride* are resinous; *bromide*, needles, m. p. 202—203° after softening at 199° (*mercuribromide*, semi-solid mass); *picrate*, m. p. 105—106° after softening at 101°.

Triphenyltelluronium Salts.—*Iodide*, m. p. 247—248° after softening from 245°; *mercuri-iodide*, small, colourless plates, which darken at 146°, soften at 155°, and are molten at about 178°; *mercuribromide*, long, colourless needles, m. p. 143—144° (decomp.); *mercurichloride*, four-sided rods, m. p. 136—137° after softening at 130° (from water), slender, silky needles, m. p. 138—139° after softening at 135° (from glacial acetic acid).

Diphenyl-o-*xylyltelluronium iodide*, microscopic cubes (+2EtOH), m. p. 114—115° with effervescence. *Diphenyl*-m-*xylyltelluronium iodide*, colourless powder, m. p. about 103° after softening at 92°; *mercuri-iodide*, colourless powder, m. p. 201—202° after softening at 195°.

Diphenyl-p-*xylyltelluronium Salts.—Iodide*, m. p. 213—214° after softening at 211°; *mercuri-iodide*, yellow, amorphous powder, m. p. about 110° after softening at 100°; *chloride*, m. p. 210—211° after softening at 207°; *mercurichloride*, m. p. about 176° after softening at 172°; *bromide*, small crystals, m. p. 207—208° after softening at 204° (from water), rods, m. p. 220—221° after softening at 218° (from alcohol–ether); *mercuribromide*, needles, m. p. 178—180° after softening at 174° (from alcohol), 174—175° after softening at 166° (from glacial acetic acid); *picrate*, small, yellow, rhombic crystals, m. p. 170—171° after softening at 168°.

Diphenyl-p-*anisyltelluronium Salts.—Iodide*, small prisms (+0·5EtOH); *mercuri-iodide*, white, amorphous powder, m. p. 89—90° after softening at 86°; the *chloride*, *bromide*, and their *mercuric* double salts are oily or resinous; *picrate*, small, yellow, monoclinic crystals, m. p. 126—127° after softening at 125°.

Diphenyl-o-*anisyltelluronium Salts.—Iodide*, colourless crystals, m. p. 230—231° after softening at 226°; *mercuri-iodide*, colourless leaflets, m. p. 218—219° after softening at 215°; the *chloride* and *mercurichloride* are resinous; *bromide*, m. p. 220—221° after softening at 215°; *picrate*, m. p. 165—166° after softening at 160—161°.

Diphenyl-m-*anisyltelluronium iodide* was obtained as a white, crystalline powder, which softened at 85° and was completely melted at about 95°; it was not isolated in the pure condition.

Diphenyl-p-*phenetyltelluronium Salts.—Iodide*, crystalline powder, m. p. about 131° after softening at 125°; *mercuri-iodide*, white, amorphous powder, m. p. 76—77° after softening at 74°.

Diphenyl-o-*phenetyltelluronium Salts.—Iodide*, m. p. 247—248° (decomp.) after softening at 225°; *mercuri-iodide*, colourless crystals, which become yellow in sunlight, m. p. about 183—184° after softening at 174°; the *chloride*, *mercurichloride*, and *picrate* form wax-like masses; *bromide*, colourless, crystalline powder, m. p. 178—179° after softening at 174°.

Diphenyl-a-naphthyltelluronium Salts.—Iodide, m. p. about 148° after softening at 130°; *mercuri-iodide*, m. p. 126° after softening at 115°; the *chloride* and *bromide* could only be isolated in an impure state.

Diphenylmesityltelluronium iodide has m. p. 153—154° after softening at 152°, whilst the *mercuri-iodide* is a white powder, m. p. 93—94° after softening at about 89°. H. W.

Tautomerism in the Triarylcarbinols: Mono-*p*-hydroxydiphenyl-α-naphthylcarbinol. M. GOMBERG and N. A. LANGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1879—1883. Compare following abstract).—*Phenyl-a-naphthyldichloromethane*, $C_{10}H_7\cdot CPhCl_2$, m. p.

92°, obtained by the action of phosphorus pentachloride on phenyl α-naphthyl ketone, when slowly added in benzene solution to a boiling solution of phenol in benzene gives *phenyl-α-naphthyldiphenoxymethane*, $C_{10}H_7\cdot CPh(OPh)_2$, m. p. 169—170°. If, however, phenol and phenyl-α-naphthyldichloromethane react together at the ordinary temperature for twelve hours and then at 50° for one hour the product is the fuchsone *phenyl-α-naphthylquinomethane*, $C_{10}H_7\cdot CPh\colon C_6H_4\colon O$, m. p. 169—170°. If this fuchsone is boiled in alcoholic solution with aqueous sodium hydroxide until the colour of the solution has changed to a light yellow, and the solution is then diluted with water and saturated with ammonium chloride, *phenyl*-p-*hydroxyphenyl-α-naphthylcarbinol*,

$$C_{10}H_7\cdot CPh(OH)\cdot C_6H_4\cdot OH,$$

is obtained in its quinonoid form, and it is not possible to isolate the benzenoid form. Thus, as in the case of its isomeride, diphenyl-4-hydroxy-α-naphthylcarbinol (*loc. cit.*), the naphthyl group exerts its tautomerising influence with the production of the quinonoid tautomeride.

When phenyl-α-naphthyldichloromethane and phenol previously saturated with dry hydrogen chloride are heated at 110° for twenty-four hours and the product, after the removal of the excess of phenol by steam distillation, is poured into 5% aqueous sodium hydroxide, 4 : 4′-*dihydroxytriphenyl-α-naphthylmethane*,

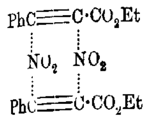
$$C_{10}H_7\cdot CPh(C_6H_4\cdot OH)_2,$$

m. p. 209—210° (decomp.), is obtained. W. G.

Tautomerism in the Triarylcarbinol Series; Diphenyl-4-hydroxy-1-naphthylcarbinol and Diphenyl-2-hydroxy-1-naphthylcarbinol. M. GOMBERG and F. W. SULLIVAN, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 1864—1870).—A quantitative yield of *p*-naphthafuchsone may be obtained by mixing together benzophenone chloride and α-naphthol in a dry atmosphere, and after leaving the mixture overnight making it slightly alkaline with dilute sodium hydroxide and distilling it with steam. On bromination in acetic acid solution the fuchsone gives 3-*bromo*-p-*naphthafuchsone*, m. p. 176°, and on chlorination 3-*chloro*-p-*naphthafuchsone*, m. p. 161°. *o*-Naphthafuchsone was similarly obtained from benzophenone chloride and β-naphthol, but in this case the addition of aluminium chloride as a catalyst was necessary. When dissolved in alcoholic sodium hydroxide and an aqueous solution of ammonium chloride added to this solution, *p*-naphthafuchsone gave almost entirely the quinonoid form of *diphenyl*-4-*hydroxy-α-naphthylcarbinol*, whilst *o*-naphthafuchsone gave exclusively the benzenoid form of *diphenyl*-2-*hydroxy*-1-*naphthylcarbinol*. The bromo- and chloro-derivatives described above gave the quinonoid forms of *diphenyl*-3-*bromo*-4-*hydroxy*-1-*naphthylcarbinol* and *diphenyl*-3-*chloro*-4-*hydroxy*-1-*naphthylcarbinol* respectively.

Both *o*- and *p*-naphthafuchsones give additive compounds with hydrogen chloride, but the chloro- and bromo-naphthafuchsones do not. W. G.

Addition of Nitrogen Peroxide to Ethyl Phenylpropiolate. HEINRICH WIELAND [with HANS WAGNER] (*Ber.*, 1920, **53**, [*B*], 1343—1346).—When nitrogen peroxide is passed into a cold solution of ethyl phenylpropiolate in light petroleum, colourless, prismatic crystals readily separate, which rapidly decompose into the original materials when filtered. Analysis of the compound is effected by the addition of an unweighed portion of the material to $N/10$-potassium hydroxide solution in the presence of ether and subsequent estimation of the ethyl phenylpropiolate and the amount of alkali used and of potassium nitrite formed. It is thus shown that one molecule of nitrogen peroxide is absorbed for each molecule of ester, and it is suggested that the molecules are united by means of the partial valencies of the acetylenic carbon atoms, as indicated by the annexed formula.



[With E. SCHAMBERG.]—When the primary labile additive compound is allowed to remain overnight in contact with light petroleum, it decomposes into ethyl phenylpropiolate and a mixture of the stereoisomeric ethyl $\alpha\beta$-dinitrocinnamates, of which the *modification*, almost colourless needles, m. p. 66·5°, has been isolated.

H. W.

Preparation of Tropic Acid from Ethyl Formylphenylacetate. JULIUS VON BRAUN (*Ber.*, 1920, **53**, [*B*], 1409).—Recently McKenzie and Wood (T., 1919, **115**, 228) have found that tropic acid can only be obtained in 16—30% yield by the reduction of ethyl formylphenylacetate with aluminium amalgam, and subsequent hydrolysis of the tropic ester. This result does not agree with the author's experience, since he finds the yield of acid to be about 50% of that theoretically possible, whilst a half of the original ester remains combined with the aluminium hydroxide, from which it can be recovered by acidification and extraction with ether. The difference is possibly to be ascribed to the use of insufficiently active aluminium amalgam.

H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXIX. Esterification of 4-Dimethylamino*iso*phthalic Acid. NIKOLA SMODLAKA (*Monatsh.*, 1920, **41**, 115—124. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76).—1-*Methyl* 3-*hydrogen* 4-*dimethylamino*iso*phthalate*, colourless prisms or crystalline powder, m. p. 180°, is formed by the esterification of the acid with methyl-alcoholic hydrogen chloride at the ordinary temperature (preparative process) or by the hydrolysis of the normal ester in boiling aqueous methyl-alcoholic solution or with boiling $N/10$-hydrochloric acid (preparative method). 3-*Methyl* 1-*hydrogen* 4-*dimethylamino*iso*phthalate*, colourless, shining leaflets, m. p. 190°, results from the esterification of the acid with methyl alcohol at 140°, from the action of methyl iodide on the normal silver or potassium hydrogen salt, and from the semi-hydrolysis of the normal

ester in methyl-alcoholic solution by means of potassium hydroxide or hydrogen chloride. The constitution of the esters is deduced from the production of the former by the esterification of the acid with methyl alcohol and hydrogen chloride, and from the behaviour of the silver salts when distilled, whereby in the first case a mixture of (?) *p*-dimethylaminobenzoic acid, m. p. 230—233°, and methyl *p*-dimethylaminobenzoate is produced, whilst in the second instance, resinous and less definite substances are formed, which could not be fully examined owing to lack of material. The experiment, however, proves that the two silver salts behave in a totally dissimilar manner when heated, and that a transformation only occurs to a slight extent if at all. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXX. Esterification of 4-Acetylamino*iso*phthalic Acid. HERMANN MEYER (*Monatsh.*, 1920, **41**, 125—138. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76, and preceding abstract).—1-Methyl 3-hydrogen 4-acetylamino*iso*phthalate, m. p. 218°, is prepared by the semi-hydrolysis of the normal ester with alkali in aqueous or methyl-alcoholic solution. The isomeric *3-methyl 1-hydrogen 4-acetylamino*isophthalate, m. p. 265°, is obtained by the action of methyl iodide on the normal silver salt in the presence of methyl alcohol (the process does not, however, occur smoothly, and yields only 20% of the normal ester, a small amount of the hydrogen ester, and mainly the unchanged acid), or on the potassium hydrogen salt (in which case also side-reactions occur, giving rise to free acid). A hydrogen ester could not be isolated from the products of the action of methyl alcohol on the acid at 100° or 120—130° or 200°, since under these conditions loss of carbon dioxide appears to take place with consequent formation of *p*-acetylaminobenzoic acid. Similarly, the hydrogen ester could not be obtained by boiling the normal ester with dilute aqueous hydrochloric acid. The constitution of the esters follows from the observation that the isomeride, m. p. 218°, is transformed by boiling acetic anhydride into methyl anhydro-4-acetylamino*iso*phthalate, m. p. 172°, and since dehydration occurs by loss of water between the acetylamino- and the adjacent carboxyl group the ester must be the 1-methyl compound.

*Silver 4-acetylamino*iso*phthalate* forms a gelatinous mass; a silver hydrogen salt could not be isolated. *Potassium hydrogen 4-acetylamino*iso*phthalate* is prepared by the addition of aqueous potassium hydroxide solution to a suspension of the acid in methyl alcohol. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXI. Esterification of 4-Methylamino*iso*phthalic Acid. JOHANN TAUB (*Monatsh.*, 1920, **41**, 139—152. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76, and preceding abstracts).—1-Methyl 3-hydrogen 4-methylamino*iso*phthalate, colourless, delicate needles, m. p. 244—245° (decomp.), is formed in

larger quantity than the isomeric *3-methyl 1-hydrogen 4-methylamino*iso*phthalate* by all the methods of esterification and semi-hydrolysis; the latter, colourless crystals, m. p. 220—221°, is prepared by the semi-hydrolysis of the normal ester or by the action of methyl iodide on the silver salt. The former isomeride seems to be the only one produced by the action of methyl-alcoholic hydrogen chloride or sulphuric acid on the acid; in the absence of mineral acid, methyl alcohol only causes slight esterification of 4-methylamino*iso*phthalic acid at 100°, whilst at 170° no trace of ester is produced, the acid losing carbon dioxide and being converted into an anthraquinone dye, which was not further investigated. The action of methyl iodide on the *potassium hydrogen* salt in the presence of methyl alcohol yields mainly the acid, together with small quantities of the normal ester and the 1-methyl 3-hydrogen ester, whilst a mixture of acid, normal ester, 1- and 3-methyl hydrogen esters (in which the former considerably predominates), is obtained from the *silver hydrogen* salt; the methylamino-group does not appear to undergo methylation during this treatment. The hydrolysis of the normal ester with methyl-alcoholic potassium hydroxide, aqueous potassium hydroxide, water, and with aqueous or methyl-alcoholic hydrochloric acid under varied conditions is described; in every case the hydrogen ester consists mainly of the 1-methyl compound, the 3-methyl isomeride being formed in subordinate amount if at all. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXII. 4-Nitro*iso*phthalic Acid and the Reduction of its Hydrogen Esters to 4-Amino*iso*phthalic Esters. PHILIPP AXER (*Monatsh.*, 1920, **41**, 153—165).—The oxidation of 4-nitro-*m*-xylene by calcium permanganate leads to the formation of a mixture of 4-nitro*iso*phthalic acid, m. p. 255—256·5° (corr.), 6-nitro-*m*-toluic acid, yellow, silky needles, m. p. 218·5—219°, and small quantities of 4-nitro-*m*-toluic acid, m. p. 133—134·5°. *Potassium hydrogen 4-nitro*iso*phthalate* is readily prepared as a white powder, sparingly soluble in water, by the mixture of solutions of equivalent amounts of the normal potassium salt and the free acid; the silver hydrogen compound could not be prepared. *Methyl 4-nitro*iso*phthalate*, yellow, rhombic crystals, $a:b:c=0·3875:0·3383:1$, m. p. 87—88·5°, is prepared in about 80% yield by the esterification of the acid with a mixture of equal volumes of concentrated sulphuric acid and methyl alcohol. *1-Methyl 3-hydrogen 4-nitro*iso*phthalate*, well-formed, colourless needles, m. p. 153·5—154° (corr.), is most conveniently prepared from the acid and methyl alcohol in the presence of a smaller proportion of concentrated sulphuric acid, and its constitution is deduced from its mode of formation. It is also obtained from the acid and methyl alcohol at 100° in the absence of mineral acid. *3-Methyl 1-hydrogen 4-nitro*iso*phthalate*, powder, m. p. 192—194° (corr.), is most conveniently prepared by the semi-hydrolysis of the normal ester either by potassium hydroxide in aqueous methyl-alcoholic solution or by aqueous methyl-

alcoholic hydrogen chloride. Potassium hydrogen 4-nitro*iso*phthalate is not methylated by treatment with methyl iodide at 100° during twenty hours. The acid is partly transformed by methyl iodide in the presence of acetone and silver oxide into the normal ester, but remains unaffected by methyl sulphate. The silver salt is quantitatively transformed by methyl iodide into the normal ester.

1-Methyl 3-hydrogen 4-nitro*iso*phthalate is reduced by tin and concentrated hydrochloric acid to 1-methyl 3-hydrogen 4-amino*iso*phthalate, m. p. 221—222° (corr.), the yield, however, being poor, and the product contaminated with much free amino-acid. Better results are obtained with the isomeric ester, which yields *3-methyl 1-hydrogen 4-amino*iso*phthalate*, colourless, crystalline powder, m. p. 228—230° (corr., slight decomp.). Methyl 4-amino*iso*phthalate, m. p. 127—129° (corr.), is similarly obtained in good yield from the normal nitro-ester. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXIII. Esterification of Aminodicarboxylic Acids. RUDOLF WEGSCHEIDER (*Monatsh.*, 1920, **41**, 167—183).—A theoretical paper which is devoted to a discussion of the results obtained during the investigation of the esterification of amino-carboxylic acids and the partial hydrolysis of their esters.

The aminodicarboxylic acids and, so far as is known, other dicarboxylic acids which contain an imino-group or nitrogen atom as a member of an open chain generally conform to the rules which have been propounded for the formation of hydrogen esters. The amino-groups must be assumed to cause steric hindrance, the unsubstituted or alkylated amino-groups to have a positive and the acylated amino-groups to have a negative action. Less regularity is observed in the semi-hydrolysis; it not infrequently happens that the action follows different courses in alcoholic and aqueous solution, but, on the other hand, it is immaterial whether hydrolysis is effected by alkali hydroxide or by hydrochloric acid. In the semi-hydrolysis of the acylated amino-esters, the influence of the strength of the carboxyl group outweighs that of steric hindrance; on the other hand, these two factors do not appear adequate to explain the course of semi-hydrolysis of the esters of unsubstituted or *N*-alkylated amino-acids, particularly in aqueous solution. With regard to the other reactions, irregularities are only observed with dimethylamino*iso*phthalic acid (action of alcohol on the acid in the absence of catalyst and of methyl iodide on the salts). It is quite possible that all these irregularities (including such as are observed during semi-hydrolysis) are to be ascribed to the participation of the amino-groups in the reactions.

The following generalisations (which are not without exception) are drawn from a consideration of the melting points of amino-*iso*- and tere-phthalic acids and their esters: (1) Methylation at the nitrogen atom depresses the melting point (exceptions occur in the methylation of methylaminoterephthalic acid, 1-methyl

3-hydrogen 4-amino*iso*phthalate, and acetylamino*iso*phthalic acid). (2) Acetylation at the nitrogen atom raises the melting point of those hydrogen esters in which the esterified carboxyl is in the ortho-position to the amino-group, but depresses it in the case of the acids (except methylamino*iso*phthalic acid), and to a slight extent in that of the acid esters of different relative position, as well as in the instances of the dimethyl esters of amino*iso*phthalic acid and methylaminoterephthalic acid. (3) Derivatives of 4-amino*iso*phthalic acid have higher melting points than the corresponding compounds derived from aminoterephthalic acid. (The dimethyl esters of the amino- and acetylamino-acids form exceptions.) (4) Among isomeric hydrogen esters of acetylated acids, the compound in which the esterified carboxyl group is adjacent to the acetylamino-group has the higher melting point; a similar irregularity is not observed with the amino- and methylamino-acids.

H. W.

Friedel and Crafts' Reaction: Nitrophthalic Anhydrides and Acetylaminophthalic Anhydrides with Benzene and Aluminium Chloride. WALTER A. LAWRANCE (*J. Amer. Chem. Soc.*, 1920, **42**, 1871—1879).—3-Nitrophthalic anhydride, when heated with benzene and aluminium chloride, gave a mixture of o'-*nitro*-o-*benzoylbenzoic acid*, m. p. 220—221° (decomp.), and m-*nitro*-o-*benzoylbenzoic acid*, m. p. 157—160° (decomp.). 2-Ethyl 1-hydrogen 3-nitrophthalate gave with thionyl chloride an *acid chloride*, m. p. 76—77°, which with benzene and aluminium chloride yielded *o'*-nitro-*o*-benzoylbenzoic acid. Similarly the *chloride* of 1-ethyl 2-hydrogen 3-nitrophthalate gave *m*-nitro-*o*-benzoylbenzoic acid. 4-Nitrophthalic anhydride when submitted to Friedel and Crafts' reaction gave *m*-nitro-*o*-benzoylbenzoic acid and *p*-nitro-*o*-benzoylbenzoic acid. Under similar conditions, 3-acetylaminophthalic anhydride yielded m-*amino*-o-*benzoylbenzoic acid*, m. p. 193—194°, and o'-*amino*-o-*benzoylbenzoic acid*, m. p. 159—160°, together with some *diphenyl*-?-*aminophthalide*, m. p. 86—89°. 4-Acetylaminophthalic anhydride gave *m*-amino-*o*-benzoylbenzoic acid and *p*-amino-*o*-benzoylbenzoic acid.

W. G.

α-Naphtholphthaleins and its Ethers. W. SCHULENBERG (*Ber.*, 1920, **53**, [*B*], 1445—1457).—As considerable doubt exists as to the constitution of the α-naphtholphthalein obtained by the condensation of phthalyl chloride with α-naphthol (compare Sörensen and Palitzsch, A., 1910, ii, 446; Copisarow and Weizmann, T., 1915, **107**, 878; Csányi, this vol., i, 54), the author has attempted the synthesis of an undoubted *oo'*-naphtholphthalein, and for this purpose has condensed α-naphtholphthaloylic acid (Deichler and Weizmann, A., 1903, i, 349) with α-naphthol in sulphuric acid solution; the product forms colourless crystals, m. p. 253—254° after previous darkening, and closely resembles the substance described by Csányi as the *pp'*-isomeride, but differs widely from the *oo'*-derivative described by Copisarow and Weizmann, to which the m. p. 209—210° is ascribed. The mode of attachment of the second naphthol group is elucidated by the conversion of

the substance into α-naphthafluoran. The same substance was also obtained in small yield by the interaction of phthalyl chloride and α-naphthol under milder conditions than those usually adopted, whilst no trace of an isomeric *p*-phthalein could be detected.

The condensation of phthalic acid with α-naphthyl ethers follows a different course. Thus phthalic anhydride and α-naphthyl methyl ether react in carbon disulphide solution in the presence of aluminium chloride to yield 4-*methoxynaphthylphthaloylic acid*, colourless, acute prisms, m. p. 194° (the *sodium* salt, rhombic plates, and *calcium* salt, prisms, $+10H_2O$, are described), which can also be prepared from phthalyl chloride and α-naphthyl methyl ether. The constitution of the acid is deduced from the extreme difficulty of effecting its demethylation, and, with greater certainty, from a comparison of its properties with those of the isomeric acid of the ortho-series. Thus the former yields a *normal* and a *pseudo-methyl* ester, colourless, rhombic plates, m. p. 96°, and needles, m. p. 120°, whilst the latter gives an *ether* ester, double pyramids, m. p. 117—119°, and an *ether acid*, colourless needles, m. p. 179°. Finally, when melted with potassium hydroxide, the acid yields 1:4-hydroxynaphthoic acid, m. p. 178°. 4-Methoxynaphthylphthaloylic acid behaves as a weak acid, and is partly liberated from its sodium salt by carbon dioxide, and cannot be titrated with sodium hydroxide in the presence of phenolphthalein as indicator; its behaviour indicates its existence in the desmotropic forms, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_6\cdot OMe$ and

$$C_6H_4<\begin{matrix}C(OH)\cdot C_{10}H_6(OMe)\\ CO\end{matrix}>O,$$

and this conception is supported by the isolation of the two methyl esters mentioned above. It suffers extensive decomposition when heated above its melting point, yielding, among other substances, α-naphthyl methyl ether, phthalic acid, α-naphthafluoran, and a substance, pale yellow, hexagonal prisms, m. p. 201—202°, which was not further identified. It condenses with α-naphthyl methyl ether in the presence of concentrated sulphuric acid to give p-*naphtholphthalein dimethyl ether*, colourless, slender needles, m. p. 246—247°, which can also be obtained in 83% yield by the prolonged interaction of phthalyl chloride and α-naphthyl methyl ether in carbon disulphide solution in the presence of a trace of aluminium chloride at the ordinary temperature. The isomeric o-*naphtholphthalein dimethyl ether* is prepared by methylation of the phthalein, and forms colourless, microscopic needles, m. p. 291°.

The results outlined above do not appear to harmonise readily with those obtained by Copisarow and Weizmann (*loc. cit.*), who find that the action of phthalyl chloride on α-naphthyl ethyl ether produces, successively, o-1-ethoxynaphthoylbenzoic acid, m. p. 155—156°, and di-1-ethoxynaphthylphthalide, m. p. 159°. The author has therefore repeated the work, and has obtained totally different results, since he finds the acid to melt at 166—167° and to have all the properties of a para-derivative, since it behaves

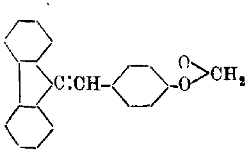
towards concentrated sulphuric acid in precisely the same manner as 4-methoxynaphthylphthaloylic acid, and is converted by fused potassium hydroxide into 4-hydroxynaphthoic acid. Further, the naphtholphthalein ethyl ether did not melt below 298°, whilst the acid was indifferent towards dealkylating agents. 1:2-Naphtholphthaloylic acid can be readily converted into o-1-*ethoxynaphthoylbenzoic acid*, irregular prisms, m. p. 145°, by treatment with ethyl sulphate and subsequent hydrolysis of the *ethyl* ester, prisms, m. p. 89°, thus produced. H. W.

Synthesis of 3 : 5-Dihydroxybenzaldehyde. F. Mauthner (*J. pr. Chem.*, 1920, [ii], **101**, 93—96).—3:5-*Dimethylcarbonatobenzaldehyde*, m. p. 154—155°, is prepared by the action of hydrogen on a solution of 3:5-dimethylcarbonatobenzoyl chloride (E. and H. O. L. Fischer, A., 1913, i, 478) in dry toluene at 110° in the presence of palladised barium sulphate. It yields a p-*nitrophenylhydrazone*, red needles, m. p. 222—223°, and is converted by aqueous sodium hydroxide and subsequent acidification into 3:5-*dihydroxybenzaldehyde*, colourless needles, m. p. 145—146°; the p-*nitrophenylhydrazone*, which completely decomposes, without melting, at 280°, and the *semicarbazone*, long needles, m. p. 223—224° (decomp.), of the latter are described.

H. W.

Preparation of Piperonaldehyde from Camphor Oil. I. and II. Shoichiro Nagai (*J. Chem. Ind. Tokyo*, 1920, **23**, 56—79, 151—172).—The fraction of camphor oil, b. p. 220—230°, contains mainly safrole, eugenol, carvacrol, cadinene, and *n*-octoic acid. By further distillation of this fraction, treatment with 25% sodium hydroxide, cooling at −19°, and adding a few crystals of safrole, safrole could be completely crystallised out. Next, when 300 c.c. of safrole are heated with 45 grams of potassium hydroxide (15 grams in each 100 c.c.) for five hours at 180—200°, 90% was changed into *iso*safrole. The method of oxidation of *iso*safrole into piperonaldehyde is discussed. Potassium dichromate and sulphuric acid gave the best yield, 47% of the theoretical value. When potassium permanganate was used, the yield was only 8%, most of the *iso*safrole being oxidised to piperonylic acid. The purification of piperonaldehyde is best effected by recrystallisation from 70% alcohol. Chemical Abstracts.

New Reaction of Aldehydes. Remo de Fazi (*Gazzetta*, 1920, **50**, ii, 146—148. Compare A., 1916, ii, 457; Guglialmelli and Delmon, A., 1918, i, 161).—Since fluorene resembles acenaphthene



in giving a reddish-violet coloration with cyclic aldehydes in presence of concentrated sulphuric acid, the author has initiated experiments to ascertain if the condensation products of fluorene with aldehydes are able to yield this coloration with the sulphuric acid. It is

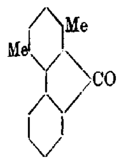
found that, in presence of sodium ethoxide, fluorene condenses at the ordinary temperature with piperonaldehyde, *m*-tolualdehyde, cuminaldehyde, *p*-dimethylaminobenzaldehyde, etc.; for instance, with piperonaldehyde, fluorene yields piperonylidenefluorene (foregoing formula). These condensation products, to be described in detail later, give the above coloration in alcoholic solution with concentrated sulphuric acid. T. H. P.

Constitution of the Salts of Aminoacetophenones. MITSURU KUHARA, HEIKICHI SAITO, and AKIRA SHIMOMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 201—215).—A study of the absorption spectra of the different salts of the three isomeric aminoacetophenones. The hydrochlorides of *o*- and *p*-aminoacetophenones both give coloured solutions in alcohol, and these coloured salts show a new absorption band in the visible region. This coloration is weakened if an excess of dry hydrogen chloride is passed through the alcoholic solution, and then the second band is no longer visible. *m*-Aminoacetophenone hydrochloride and *p*-dimethylaminoacetophenone hydrochloride do not give coloured salts, and their alcoholic solutions do not give an extra absorption band. It is considered that the coloured ortho- and para-salts are the quinonoid form and the colourless salts the benzenoid form, the change from one form to the other being of the keto-enol type.

p-Dimethylaminoacetophenone, m. p. 105°, was prepared by heating *p*-aminoacetophenone and methyl iodide in aqueous sodium hydroxide for several hours. It gave a *hydrochloride*, m. p. 147—148° (decomp.), and a *picrate*, m. p. 124° (decomp.). W. G.

Preparation of 1 : 4-Dimethylfluorenone and Attempts to Transform it into a Derivative of Phenanthrone. ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1920, **53**, [*B*], 1388—1398. Compare Schaarschmidt, A., 1917, i, 275). —Various attempts to synthesise *o*-aminophenyl *p*-xylyl ketone are described. Thus, 2-p-*toluenesulphonylaminophenyl* p-*xylyl ketone*, $C_6H_3Me_2\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_4Me$, small, colourless crystals, m. p. 107—108°, was prepared by the successive action of phosphorus pentachloride and aluminium chloride on *p*-toluenesulphonylanthranilic acid in the presence of *p*-xylene, but the *p*-toluenesulphonyl group could not be smoothly removed. Similarly, *p*-xyloyl-*o*-benzoic acid was converted successively into the chloride and *amide*, colourless needles, m. p. 149—150°, which could not be transformed into the amine in a satisfactory manner. Attempts to prepare *o*-nitrophenyl *p*-xylyl ketone by the action of *o*-nitrobenzoyl chloride on *p*-xylene in the presence of aluminium chloride and carbon disulphide were unsuccessful, resinous products being obtained. Finally, o-*bromophenyl* p-*xylyl ketone*, colourless, shining leaflets, m. p. 46°, was converted by alcoholic ammonia at 180—190° into o-*aminophenyl* p-*xylyl ketone*, mainly obtained as a yellow oil which decomposed completely when distilled; from

this, however, small amounts of pale yellow crystals, m. p. 76—78° to a cloudy liquid, which suddenly became transparent at 88—90°, could be isolated. It was converted by diazotisation and subsequent treatment with copper powder into o-*hydroxyphenyl* p-*xylyl ketone* (yellowish-brown, viscous mass, which was not further investigated), 2:5-dimethylbenzophenone, b. p. 312—314°/ atmospheric pressure, and 1:4-*dimethylfluorenone* (annexed formula), long, yellow needles, m. p. 108°. When fused with potassium hydroxide, the latter yields an *acid*, colourless needles, m. p. 145° (the *silver* salt is described), which, since it is not esterified by cold saturated methyl-alcoholic hydrogen chloride, and yields 1:4-dimethylfluorenone when treated with concentrated sulphuric acid, is considered to be 2:5-dimethyldiphenyl-6-carboxylic acid.



The fission of substituted ring ketones under the influence of molten alkali hydroxide appears to take place quantitatively in one direction only, and the position occupied by the carboxyl group depends on the substituent already present. If the latter is acidic in character, the new carboxyl group becomes located in the unsubstituted benzene nucleus; if, however, it is basic ($-NH_2$ or $-OH$), the new group is attached to the already substituted nucleus. The latter seems also to be the case when a methyl radicle is in the ortho-position. H. W.

Anthracene. VI. Desmotropy of the Reduction Products of Hydroxyanthraquinones. KURT H. MEYER and ALBERT SANDER (*Annalen*, 1920, **420**, 113—125. Compare A., 1911, i, 193).—An investigation of the effect of the introduction of hydroxy-groups on the equilibrium between anthrone and anthranol forms.

The reduction of 1-hydroxyanthraquinone to a substance considered to be 1-hydroxyanthranol has been described by the Höchst Farbwerke (D.R.-P. 242053); the absence of fluorescence from the alcoholic solution and failure of the substance to combine with bromine show it to be in reality 1-hydroxyanthrone, and this conception explains the observed ability of the compound to condense with isatin chloride or anilide, with the production of indigoid dyes containing the new group in the side nucleus. In alcoholic solution, equilibrium is attained in the presence of 3—4% of hydroxyanthranol. With 1:9-dihydroxyanthrone and 1-hydroxyanthraquinol, equilibrium is set up when about 10% of the latter is present. In the cases of 1:4-dihydroxyoxanthrone and 1:4-dihydroxyanthraquinol, the latter is found to pass with great readiness into the former, so that it appears, in general, that the tendency towards ketone formation is increased by the entrance of hydroxyl groups in the α-position in the side nucleus.

The following individual substances are described: 1:9-*anthranylene diacetate*, $C_6H_4<\overset{C(OAc)}{\underset{CH\text{-}\!\!-\!\!-}{|}}>C_6H_3(OAc)$, colourless or pale yellow needles, m. p. 148—149°; the *dibenzoate*, yellow

needles, m. p. 191° (from α-hydroxyanthrone and the requisite acid chloride in the presence of pyridine); 9-*bromo*-1-*hydroxyanthrone*, $C_6H_4<\substack{CO\\CHBr}>C_6H_3\cdot OH$, yellow needles, m. p. 273° (decomp.) after softening and darkening from 130°, which readily loses hydrogen bromide, and, on treatment with copper powder, gave a *substance*, m. p. 188—189°; 1:9-*dihydroxyanthrone*, $C_6H_4<\substack{CO\\CH(OH)}>C_6H_3\cdot OH$, deep yellow needles, m. p. 135—137° (from the bromo-compound and aqueous acetone); 1-*hydroxyanthraquinol*, dark olive-green needles, m. p. 204—206°, which undergoes autoxidation with extreme ease; 1:4:9-trihydroxyanthrone, $C_6H_4<\substack{CO\\CH(OH)}>C_6H_2(OH)_2$, m. p. 157—158° after previous softening, which is best obtained by reducing a solution of quinizarin in glacial acetic acid with tin and hydrochloric acid, and which has been considered by Liebermann to be 1:4-dihydroxyanthraquinol; the latter *substance*, prepared by reduction of quinizarin with zinc dust in alkaline solution and subsequent acidification, has m. p. 131—136°, readily undergoes autoxidation, passes into the ketonic form when recrystallisation is attempted, and is oxidised by an alcoholic solution of bromine to quinizarin.

Purpurin, when subjected to reduction, is converted into leucopurpurin and a substance, $C_{14}H_{10}O_5$, m. p. 162—163°, which is transformed in alkaline solution into quinizarin, and has hence been termed leucoquinizarin I. It is now shown that it is produced when leucopurpurin is boiled in acetic acid solution, that it is stable towards air and indifferent to an alcoholic solution of bromine, and, further, that its conversion into quinizarin by sodium hydroxide occurs in complete absence of air. It therefore appears to be 2-hydroxy-1:4-diketo-1:2:3:4-tetrahydroanthraquinol, and to be formed by the passage of leucopurpurin into the ketonic form, the subsequent production of quinizarin being due to the loss of water.

Liebermann's β-hydroxyanthranol has been further examined, but definite conclusions as to the desmotropic relationships cannot yet be drawn; the stable modification, however, appears to be enolic. H. W.

Anthracene. VII. The Alkylation of Anthranol. Kurt H. Meyer and Hans Schlösser (*Annalen*, 1920, **420**, 126—133).—In continuation of previous work (A., 1911, i, 195), the authors have studied the alkylation of anthranol by alkyl sulphates and alkyl haloids respectively. The former shows the greater tendency towards the formation of O-ethers by direct exchange of the alkyl group for the metallic atom, whereas the latter cause alkylation in the nucleus to a much more pronounced extent. It is suggested that a part of the alkyl haloid is added at the active double bond of anthranol, yielding 9-alkylanthrone, which is transformed in the alkaline solution into 9-alkylanthranol; the latter can then react

further with alkyl haloid, one portion of it giving the O-ether, whilst another portion adds alkyl haloid and yields dialkylanthrone.

Anthranol methyl ether, $C_6H_4<\begin{smallmatrix}C(OMe)\\|\\CH\end{smallmatrix}>C_6H_4$, coarse leaflets, m. p. 94°, is prepared by the action of methyl sulphate and alkali on an alcoholic solution of anthrone; when dissolved in boiling benzene and treated with phosphorus pentachloride, it yields 10-*chloroanthranol methyl ether*, yellow crystals, m. p. 154°, whilst with bromine in carbon disulphide solution it gives 10-*bromoanthranol methyl ether*, colourless crystals, m. p. 145°. When treated with aqueous potassium hydroxide and methyl iodide, anthrone is mainly converted into *methylanthranol methyl ether*, $C_6H_4<\begin{smallmatrix}C(OMe)\\|\\CMe\end{smallmatrix}>C_6H_4$, m. p. 147°, together with very small quantities of dimethylanthrone, m. p. 95°, which, according to the older observations of Hallgarten, is the main product of the change. Methylanthranol methyl ether is transformed by bromine in carbon disulphide solution into ω-9-*dibromomethylanthrone*,

$$C_6H_4<\begin{smallmatrix}CO\\CBr(CH_2Br)\end{smallmatrix}>C_6H_4,$$

yellow crystals, m. p. 135—140° (decomp.) after darkening at 120°, the constitution of which is deduced from its formation from methyleneanthraquinone and bromine (following abstract).

With ethyl sulphate and alkali, anthrone gives *anthranol ethyl ether*, yellow plates, m. p. 73°, which yields a very unstable bromo-derivative, and is converted by amyl nitrite in acetic acid solution containing a little hydrochloric acid into anthraquinoneoxime. In agreement with Goldmann's data, anthranol is converted by ethyl iodide into diethylanthrone, m. p. 135°, and 9-ethylanthranol ethyl ether, m. p. 84°.

Anthrone is transformed by aqueous methylamine solution into N-*methyl*meso*anthramine*, $C_6H_4<\begin{smallmatrix}C(NHMe)\\|\\CH\end{smallmatrix}>C_6H_4$, sulphur-yellow needles, m. p. 90° after softening at 85°; the *hydrochloride* forms pale yellow crystals, m. p. 225°. The action of methyl iodide on the base gives only unchanged material and anthraquinone, whilst the latter is obtained when methyl sulphate is used. H. W.

Anthracene. VIII. Methyleneanthraquinone. KURT H. MEYER (*Annalen*, 1920, **420**, 134—136).—Simple methylenequinones have been somewhat frequently described in the literature, but several of them have been shown by Pummerer and Cherbuliez (A., 1915, i, 419) to be dehydrophenols, whilst, more recently (A., 1919, i, 439), Pummerer has expressed the opinion that the remainder are more complex substances, which are probably also to be regarded as dehydrophenols. The author has now succeeded in isolating *methyleneanthraquinone*, $C_6H_4<\begin{smallmatrix}CO\\C(:CH_2)\end{smallmatrix}>C_6H_4$, by the condensation of a cold alkaline solution of anthranol with an excess of formaldehyde. It forms stable, pale yellow prisms, m. p. 148°, and

instantaneously adds bromine in carbon disulphide solution, yielding bromomethylbromoanthrone, m. p. 135—140° (decomp.) after becoming discoloured at 110°, identical with the product obtained by the bromination of methylanthranol methyl ether (preceding abstract). H. W.

Rotatory Dispersion of the Menthyl Esters of certain Keto-acids. H. RUPE and H. KÄGI (*Annalen*, 1920, **420**, 33—84). —The present communication describes an extension of the work of Rupe and Lenzinger (A., 1913, i, 266, 884), who prepared a number of the esters, but only observed their specific rotations for the sodium *D*-line. The rotatory dispersions are now recorded. The following substances are described.

Menthyl cyanoacetate, m. p. 83·5°, $[\alpha]_{C}^{20}$ −64·15°, $[\alpha]_{D}^{20}$ −80·92°, $[\alpha]_{Hg}^{20}$ −95·21°, $[\alpha]_{F}^{20}$ −123·57° in benzene solution. Menthyl phenylpropiolate, m. p. 63—64°, $[\alpha]_{C}^{20}$ −57·31°, $[\alpha]_{D}^{20}$ −72·56°, $[\alpha]_{Hg}^{20}$ −85·9°, $[\alpha]_{F}^{20}$ −111·92° in benzene. Menthyl ethylacetoacetate, $[\alpha]_{C}^{20}$ −50·59°, $[\alpha]_{D}^{20}$ −63·85°, $[\alpha]_{Hg}^{20}$ −75·60°, $[\alpha]_{F}^{20}$ −98·39°. *Menthyl diethylacetoacetate*, b. p. 161°/9·5 mm., D_4^{20} 0·9638, $[\alpha]_{C}^{20}$ −44·35°, $[\alpha]_{D}^{20}$ −55·68°, $[\alpha]_{Hg}^{20}$ −65·53°, $[\alpha]_{F}^{20}$ −84·35° in substance, $[\alpha]_{C}^{20}$ −40·39°, $[\alpha]_{D}^{20}$ −50·77°, $[\alpha]_{Hg}^{20}$ −59·46°, $[\alpha]_{F}^{20}$ −76·50° in benzene. *Menthyl* iso*propylacetoacetate* (from menthyl sodioacetoacetate and *iso*propyl iodide in the presence of toluene at 120—125°), b. p. 158—159°/9 mm., D_4^{20} 0·9603, $[\alpha]_{C}^{20}$ −48·69°, $[\alpha]_{D}^{20}$ −61·53°, $[\alpha]_{Hg}^{20}$ −72·91°, $[\alpha]_{F}^{20}$ −95·05° in substance, $[\alpha]_{C}^{20}$ −47·32°, $[\alpha]_{D}^{20}$ −59·74°, $[\alpha]_{Hg}^{20}$ −70·58°, $[\alpha]_{F}^{20}$ −91·70° in benzene. *Ethyl diphenylmethylacetoacetate*, $CH_3 \cdot CO \cdot CH(CHPh_2) \cdot CO_2Et$, small, shining rods, m. p. 89—90°. Menthyl diphenylmethylacetoacetate could not be obtained from menthol and the ethyl ester or from menthyl acetoacetate and diphenylbromomethane and alcoholic sodium ethoxide. Reaction could be caused to occur between menthyl sodioacetoacetate and diphenylbromomethane in the presence of dry benzene, giving a product which is resolved into diastereoisomerides by prolonged fractionation; l-*menthyl* d-*diphenylmethylacetoacetate* has m. p. 118°, $[\alpha]_{C}^{20}$ −33·83°, $[\alpha]_{D}^{20}$ −41·94°, $[\alpha]_{Hg}^{20}$ −48·18°, $[\alpha]_{F}^{20}$ −60·00°, whilst *l*-menthyl *l*-diphenylmethylacetoacetate has m. p. 90°, $[\alpha]_{C}^{20}$ −51·13°, $[\alpha]_{D}^{20}$ −65·15°, $[\alpha]_{Hg}^{20}$ −78·04°, $[\alpha]_{F}^{20}$ −103·94°, and l-*menthyl* dl-*diphenylmethylacetoacetate* has $[\alpha]_{C}^{20}$ −42·62°, $[\alpha]_{D}^{20}$ −53·69°, $[\alpha]_{Hg}^{20}$ −63·31°, $[\alpha]_{F}^{20}$ −82·43°. The rotatory dispersion curves of the diastereoisomerides differ widely from one another, and the $d+l$-form exhibits complex anomaly. Somewhat similar experiences are encountered with the benzylacetoacetic esters (compare Rupe and Lenzinger, *loc. cit.*); the most readily isolable ester is l-*menthyl* l-*benzylacetoacetate*, m. p. 68°, $[\alpha]_{C}^{20}$ −94·05°, $[\alpha]_{D}^{20}$ −121·21°, $[\alpha]_{Hg}^{20}$ −145·67°, $[\alpha]_{F}^{20}$ −196·73°, whilst l-*menthyl* dl-*benzylacetoacetate*, m. p. 48—51°, $[\alpha]_{C}^{20}$ −43·43°, $[\alpha]_{D}^{20}$ −55·10°, $[\alpha]_{Hg}^{20}$ −65·20°, $[\alpha]_{F}^{20}$ −85·85°, is also obtained; the *l*-Menthyl *d*-ester could not be isolated in the pure condition. *l*-Menthyl benzylideneacetoacetate (from benzaldehyde and *l*-menthyl acetoacetate in the presence of hydrogen chloride, thus giving the *hydrochloride*, needles, m. p. 118°, as intermediate product) has $[\alpha]_{C}^{20}$ −8·17°, $[\alpha]_{D}^{20}$ −10·97°, $[\alpha]_{Hg}^{20}$ −13·66°, $[\alpha]_{F}^{20}$ −21·27° in benzene solution. l-*Menthyl diacetylacetoacetate*, colourless, odourless oil, b. p. 172—173°

11 mm., D_4^{20} 1·0239 (the pale blue *copper* salt was analysed), has $[\alpha]_C^{20}$ −61·49°, $[\alpha]_D^{20}$ −79·56°, $[\alpha]_{Hg}^{20}$ −96·34°, $[\alpha]_F^{20}$ −131·32° in substance, $[\alpha]_C^{20}$ −51·84°, $[\alpha]_D^{20}$ −66·88°, $[\alpha]_{Hg}^{20}$ −80·68°, $[\alpha]_F^{20}$ −110·64° in benzene solution. Attempts to prepare *l*-menthyl benzoylacetoacetate were unsuccessful. Menthyl benzoylacetate has $[\alpha]_C^{20}$ −50·95°, $[\alpha]_D^{20}$ −64·39°, $[\alpha]_{Hg}^{20}$ −76·15°, $[\alpha]_F^{20}$ −99·89° in benzene, whilst under similar conditions *l*-menthyl benzoylbenzylideneacetate has $[\alpha]_C^{20}$ −61·75°, $[\alpha]_D^{20}$ −78·62°, $[\alpha]_{Hg}^{20}$ −93·69°, $[\alpha]_F^{20}$ −123·84°. Menthyl *l*-benzoylcinnamylacetate, $CHPh:CH\cdot CH_2\cdot CHBz\cdot CO_2\cdot C_{10}H_{19}$ (Rupe and Lenzinger, *loc. cit.*), has $[\alpha]_C^{20}$ −67·41°, $[\alpha]_D^{20}$ −86·08°, $[\alpha]_{Hg}^{20}$ −102·18°, $[\alpha]_F^{20}$ −135·71°, but the diastereoisomeric ester could not on this occasion be isolated in a sufficiently pure condition for polarimetric investigation Menthyl *d*-benzoylphenylacetate has $[\alpha]_C^{20}$ +13·73°, $[\alpha]_D^{20}$ +21·10°, $[\alpha]_{Hg}^{20}$ +28·58°, $[\alpha]_F^{20}$ +49·91° in benzene, $[\alpha]_C^{20}$ −43·89°, $[\alpha]_D^{20}$ −58·91°, $[\alpha]_{Hg}^{20}$ −75·08°, $[\alpha]_F^{20}$ −93·57° in alcohol with one drop of piperidine. The dextrorotation is caused by the activity of the asymmetric complex of the acid preponderating over that of the menthol; in alcoholic solution, however, the ketonic rapidly passes into the enolic form, thus destroying the asymmetry of the carbon atom in the acid portion of the molecule and leaving an activity entirely due to the presence of the menthyl group. *Menthyl dibenzoylacetate*, colourless needles, m. p. 138·5—139°, has $[\alpha]_C^{20}$ −49·58°, $[\alpha]_D^{20}$ −64·07°, $[\alpha]_{Hg}^{20}$ −76·88°, $[\alpha]_F^{20}$ −104·18° in benzene.

The ethyl menthyl acetylsuccinates have also been investigated. The *α-ester*, $CO_2Et\cdot CH_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19}$, prepared from menthyl acetoacetate and ethyl chloroacetate in the presence of alcoholic sodium ethoxide, has b. p. 192—195°/9 mm., 111—112°/0·1 mm., D_4^{20} 1·0295, $[\alpha]_C^{20}$ −44·76°, $[\alpha]_D^{20}$ −56·67°, $[\alpha]_{Hg}^{20}$ −67·24°, $[\alpha]_F^{20}$ −87·97° in substance, $[\alpha]_C^{20}$ −45·59°, $[\alpha]_D^{20}$ −57·80°, $[\alpha]_{Hg}^{20}$ −67·99°, $[\alpha]_F^{20}$ −89·38° in benzene solution; the *β-ester*, $CO_2Et\cdot CHAc\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$, from menthyl chloroacetate and ethyl sodioacetoacetate, is a colourless, viscous oil, b.p. 200—202°/12 mm., 116—117°/*ca.* 0·1 mm., D_4^{20} 1·0267, $[\alpha]_C^{20}$ −38·77°, $[\alpha]_D^{20}$ −48·80°, $[\alpha]_{Hg}^{20}$ −57·45°, $[\alpha]_F^{20}$ −74·02° in substance, $[\alpha]_C^{20}$ −40·94°, $[\alpha]_D^{20}$ −51·59°, $[\alpha]_{Hg}^{20}$ −60·68°, $[\alpha]_F^{20}$ −78·29° in benzene. The product obtained by heating a mixture of menthol and ethyl acetylsuccinate is a mixture of 90% of the α- with 10% of the β-ester.

The enol content of several menthyl esters has been determined by Meyer's method of titration with bromine. The following percentages of enol are thus found, the figures for the corresponding ethyl esters being placed within brackets: menthyl acetoacetate, 17·37% (7·71%); menthyl ethylacetoacetate, 1·69% (3·1%); menthyl diacetylacetate, 72·72% (90%); menthyl acetylsuccinate, 0·65% (3·7%). Menthyl benzoylacetoacetate and menthyl benzoylphenylacetate do not unite with bromine.

On the basis of the present and previous communications, the authors are led to distinguish four types of abnormal rotatory dispersion: (i) total anomaly of a mixture of two substances with opposed activities (Tschugaev's extramolecular anomalous dispersion); (ii) total anomaly of a compound containing two different asymmetric complexes, one of which is dextro-, the other lævo-rotatory (Tschugaev's intramolecular anomalous dispersion); (iii) the

rotatory dispersion curve does not pass through a maximum or minimum, neither does it approximate to a horizontal line, but λ_a and λ_0^2 differ widely from the normal values and $\frac{1}{[\alpha]}/\lambda^2$ gives bent or zig-zag lines (complex rotatory dispersion of Lowry and Dixon); (iv) apparently normal course of the curves and $\frac{1}{[\alpha]}/\lambda^2$ gives straight lines, but λ_a and λ_0^2 differ greatly (at least $\pm 15\ \mu\mu$ for the former) from the normal value for the particular class of compound (relative anomaly).

The paper contains a criticism of the proposal by Lowry and Abram (T., 1919, **115**, 300) to delete the "relatively abnormal" classification; the author considers that sufficient substances are known, in which λ_a differs by 15—60 $\mu\mu$ and λ_0^2 by as much as five units from the normal figures for the class of substance without, however, exhibiting complex anomaly, to justify a separate classification. H. W.

The Alcohols of the Hydroaromatic and Terpene Series. III. *iso*Pulegol. ROBERT HOWSON PICKARD, HAROLD HUNTER, WILLIAM LEWCOCK, and HANNAH SMITH DE PENNINGTON (T., 1920, **117**, 1248—1263).

1-Hydroxy-2-benzoylcamphor. A. L. W. E. VAN DER VEEN (*Zeitsch. Kryst. Min.*, 1920, **55**, 627).—Colourless, sharply developed crystals 1 cm. across were crystallised from a warm solution in light petroleum. D 1·242; m. p. 95°. The symmetry-class is rhombic-bisphenoidal, as shown by the distribution of the faces and by etching; $a:b:c = 0·6535:1·0247:1$. Optical data are given. Owing to the strong dispersion of the optic axes, brilliant colours are seen in parallel light between crossed nicols when viewed along an optic axis. L. J. S.

Essential Oil of Perylla nankinensis, Dene. SEIJI FURUKAWA and ZENJIRÔ TOMIZAWA (*J. Chem. Ind. Tokyo*, 1920, **23**, 342—363).—The formation, distribution, transformation, and chemical composition of the essential oil of *Perylla nankinensis*, Dene, were investigated. The oil and its parent substance (glucoside) are formed in the leaves only, but are later transported to the ear, and radiate from the sepals, the radiation being the most active during the flowering time. Both the oil and glucosides accumulate in the leaves gradually until the ears appear, and then remain constant until the beginning of the flowering time. With the appearance of the ears, the glucosides begin to decompose, finally disappearing after flowering. The oil distilled from the fresh plants at different stages of growth shows a gradual increase in aldehydes and decrease in ester until the end of the flowering time, whilst the oil from dried plants shows the reverse. The solubility of the oil decreases with the growth of the plants. To convert the glucosides into oil, the plants must be dried at low temperature to avoid decomposition of enzyme, which causes

resinification and decrease of solubility of the oil. The essential oils contain 20—30% of *l*-limonene, 44—57% of perillaldehyde, and a little α-pinene. The various derivatives of perillaldehyde were prepared and their properties studied. Perillaldehyde has b. p. 237°, D^{15} 0·9675, $[\alpha]_D^{20}$ −145·8°. The α-*anti*-aldoxime of the aldehyde, colourless crystals, has m. p. 102°, and is exceedingly sweet, being two thousand times as sweet as sugar and four to eight times as sweet as saccharin. The hydrochloride of the oxime, unstable, white crystals, has m. p. 114°. The β-syn-*aldoxime*, colourless, triclinic prisms, has m. p. 129°, and is not sweet. The phenylhydrazone, silky needles, and semicarbazone, colourless crystals, have m. p. 107·5° and 190—199° respectively. Perillonitrile, C_9H_{13}·CN, has b. p. 123°/15 mm. and D^{15} 0·9488—0·9490, and is one-half as sweet as saccharin. Perillic acid, m. p. 132—133°, yields an amide, C_9H_{13}·CO·NH_2, colourless crystals, m. p. 164—165°. Perilla alcohol, b. p. 118—121°/11 mm., D 0·9690, forms an acetate, b. p. 123—124°/13 mm., D 0·9800.

CHEMICAL ABSTRACTS.

p-Cymene as a Solvent. A. S. WHEELER (*J. Amer. Chem Soc.*, 1920, **42**, 1842—1846).—Spruce turpentine consists largely of *p*-cymene, and for the isolation of the latter, air at the ordinary temperature is first drawn through the turpentine for ten hours, and then the turpentine is distilled with superheated steam in an apparatus arranged so that the vapours pass first through a 30% solution of sodium hydroxide and then into the condenser. The distillate is purified by shaking it with a 5% solution of sodium hydroxide, and then distilling it over sodium. So prepared, *p*-cymene has b. p. 176—176·5° and $n^{12\cdot5}$ 1·4905.

The solubilities of a whole series of organic compounds in this solvent have been determined, and are tabulated. Pure *p*-cymene containing a trace of *p*-anisidine only slowly turns yellow when exposed to light, whereas an impure specimen turns red. W. G.

The Acceleration of Vulcanisation. I. D. F. TWISS and S. A. BRAZIER (*J. Soc. Chem. Ind.*, 1920, **39**, 125—132T).—The temperature-coefficient for the vulcanisation process has approximately the same value for a mixture of rubber and sulphur as for a similar mixture containing aldehyde-ammonia as catalyst. The progress of the reaction is illustrated by curves representing the rate of attainment of a maximum tensile strength, the gradual decrease in extensibility, and the increase in the proportion of sulphur in combination with the rubber. Results are quoted of experiments using other substances as catalysts, and it is shown that *m*-phenylenediamine is less active than *p*-phenylenediamine.

D. F. T.

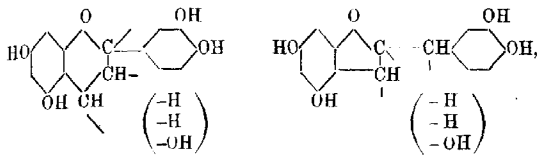
The Acceleration of Vulcanisation. II. A Discontinuity in the Effect of Vulcanisation. D. F. TWISS and C. W. H. HOWSON (*J. Soc. Chem. Ind.*, 1920, **39**, 287—289T).—The effect of 1% of "light" magnesium oxide in accelerating

vulcanisation is approximately equal to that of 0·5% of potassium hydroxide introduced as a solution in glycerol. Mercuric oxide also exerts a distinct catalytic effect. When 1% of hexamethylenetetramine is used as a catalyst in the presence of 1% of zinc oxide, the extensibility of the rubber does not decrease steadily, in the normal manner with progressive vulcanisation, but, after an initial decrease, suddenly begins to increase; after a brief period of this abnormal behaviour, a maximum is attained, and the rubber then resumes the normal decrease in extensibility. D. F. T.

Constitution of Catechin. II. MAXIMILIAN NIERENSTEIN (T., 1920, **117**, 1151—1156).

Tannins. V. Phloroglucinol Tannins and Catechins. Constitution of Gambier Catechu. KARL FREUDENBERG (*Ber.*, 1920, **53**, [*B*], 1416—1427).—The author classifies as catechins a number of substances which contain two benzene nuclei, one of which is phloroglucinol, whilst the other varies, but is commonly catechol. They are distinguished from the flavone dyes and anthocyanidins by a higher hydrogen content. They are colourless, form colourless lead salts, and do not unite with mineral acids. They are sparingly soluble in cold, freely in hot, water. They give the pine-shaving reaction with phloroglucinol and yield characteristic azobenzene derivatives. Their most characteristic property is their ability, in the presence of ferments or mineral acids in hot aqueous solution, or even when dried, both in presence and absence of atmospheric oxygen, to condense to amorphous tannins, the simpler members of which are colourless and soluble in water, whilst the more complex derivatives are insoluble and more or less coloured. This classification includes, not only the three ordinary catechins, but also substances such as cyanomaclurin, aromadendrin, colatin, cacaole, and others. When, now, the catechins are grouped together as phloroglucinol tannins, their behaviour is found to vary from member to member in precisely the same manner as that of the nearly related flavone dyes, anthocyanidins, and phenyl styryl ketones, so that the whole series appears to be similarly constituted. It is therefore the more remarkable that the only catechin which has been closely investigated should have had a formula assigned to it (von Kostanecki, A., 1907, i, 73, 334; 1908, i, 86) widely different from that of the natural dyes mentioned above, since it is considered to be derived from an ethyldiphenylmethane, whilst the latter are derivatives of $\alpha\gamma$-diphenylpropane. By the action of sodium and alcohol on catechin tetramethyl ether, followed by further methylation, von Kostanecki has obtained a pentamethyl ether which he considered to be 2 : 4 : 6-trimethoxy-3-ethylphenyl-3′ : 4′-dimethoxyphenylmethane, but which is now shown to be pentamethoxy-$\alpha\gamma$-diphenylpropane. Von Kostanecki's formula for Gambier catechu is therefore abandoned in favour of one of the alternative formulæ,

of which the author inclines to the latter, since the colour reactions of the tetramethyl ether resemble those of the coumarans.



The preparation of veratraldehyde from protocatechualdehyde is fully described, as is also that of phloroglucinol trimethyl ether (the latter is conveniently obtained by preliminary treatment of phloroglucinol with methyl alcohol and hydrogen chloride, followed by complete methylation with methyl sulphate or by the action of heat on trimethylcarbonatophloroglucinol, b. p. 195—200°/ Volmer pump vacuum). The phloroglucinol ether is converted into trimethylphloroacetophenone, which condenses with veratraldehyde to 2:4:6-trimethoxyphenyl 3′:4′-dimethoxystyryl ketone (compare Tutin and Caton, T., 1910, **97**, 2062). On reduction with hydrogen in the presence of platinum, the unsaturated ketone is reduced to 2:4:6:3′:4′-pentamethoxy-$\alpha\gamma$-diphenylpropane, colourless, rectangular crystals, m. p. 87—88°, which is identical in all respects with the ether obtained from Gambier catechu by Kostanecki and Lampe (*loc. cit.*), for which, however, these authors found a somewhat lower melting point (compare Nierenstein, T., 1920, **117**, 971, 1151). H. W.

Lignin. III. Preparation of a Tannic Acid from the Lignosulphonic Acids. Max Hönig and Walter Fuchs (*Monatsh.*, 1920, **41**, 215—222. Compare this vol., i, 291).—When aqueous solutions of the barium salts of the three fractions of the lignosulphonic acids are boiled with saturated barium hydroxide solution, they yield insoluble precipitates and readily soluble substances. The former differ from one another, and their composition has not yet been elucidated; they are all readily oxidised by alkaline permanganate, but the only product which could be characterised definitely was oxalic acid, obtained from the first fraction. The soluble *substances*, on the other hand, appear to be identical with one another, and the analytical results are in agreement with the formula $C_{18}H_{30}O_{10}SBa$, so that they are probably derived from an acid, $OMe{\cdot}C_{16}H_{27}O_4(SO_3H){\cdot}CO_2H$. The aqueous solution of the salt gives greenish-grey, green, and white precipitates with iron chloride, copper chloride, and lead acetate respectively, and voluminous precipitates with quinine hydrochloride and gelatin; it is almost quantitatively precipitated by formaldehyde and hydrochloric acid. About 70% of it is absorbed

from acid solution by hide powder. The substance therefore has all the properties of a tannic acid of the catechu group, with such modifications as are caused by the sulphur content; when fused with potassium hydroxide, it gives protocatechuic acid in good yield. H. W.

Thionaphthen in Coal Tar. R. WEISSGERBER and O. KRUBER (*Ber.*, 1920, **53**, [*B*], 1551—1565).—The presence of thionaphthen in coal tar has frequently been suspected, particularly since its investigation by Gattermann and Lockhardt (A., 1894, i, 92), and subsequently by Bezdrik, Friedländer, and Koeniger (A., 1908, i, 200), has shown that it is extraordinarily like naphthalene, but up to the present all the efforts which have been made to identify it have been unsuccessful. This, however, has now been accomplished in the following manner, the method adopted being in the first instance similar to that used by V. Meyer for the isolation of thiophen. Crude naphthalene is sulphonated with a greatly deficient amount of sulphuric acid at 90—100°, and the sulphonated product is decomposed with steam in the presence of a little sulphuric acid at 145°. The product has m. p. about 73° and contains 2—3% of sulphur. Repetition of the process gives a material containing about 5—6% of sulphur, which can be increased to 12—14% by freezing out the naphthalene. The product obtained in this manner is dissolved in glacial acetic acid and treated with hydrogen peroxide, when thionaphthen-S-dioxide, long needles, m. p. 142°, is obtained, which is identical in all respects with the synthetic product. The actual isolation of thionaphthen from "enriched" naphthalene has been effected by the use of Friedländer's mercuric acetate method (*loc. cit.*), but it is essential to guard against undue rise in temperature during the action, which can be readily effected by working with methyl-alcoholic solutions. By a similar process of partial sulphonation, followed by use of mercuric acetate, it has been found possible to isolate thionaphthen from technical "pure" naphthalene (containing 0·3—0·4% S), about 2 grams of the substance being obtained from 80 kilos. of naphthalene.

The industrial preparation of thionaphthen from crude naphthalene has also been investigated. It is found that thionaphthen is converted by sodium at 100—120° into a yellowish-brown sodium compound, which can readily be freed from adherent impurities by washing with benzene, and which decomposes, with re-formation of thionaphthen, when treated with ice-cold water; the yields, however, leave much to be desired, and the heating requires to be very carefully regulated. Far better results are obtained when sodamide is used (in the proportion of two molecules to one molecule of thionaphthen); reaction is complete at 120°, and practically the whole of the thionaphthen is liberated by water, the simultaneous formation of sodium sulphide appearing to be avoided. The process is applicable to "enriched"

naphthalene, and it is further found that the pre-formed sodamide may with advantage be replaced by sodium and dry ammonia.

The constitution of the sodium compound is discussed, but a definite conclusion is not reached. The possible desmotropic forms all contain a reactive methylene group, the presence of which cannot be established by the usual reagents, such as aromatic aldehydes, nitrous acid, or ethyl oxalate, which are indifferent towards thionaphthen. Under special conditions, however, the latter reacts with magnesium ethyl bromide, giving a compound, which is decomposed by carbon dioxide into thionaphthen-2-carboxylic acid, m. p. 236° (see later). At least one hydrogen atom must therefore be regarded as labile, and it must be assumed that the presence of the sulphur atom thus influences the neighbouring hydrogen atom, since substitution occurs preferably, and sometimes exclusively, in this position.

The action of carbon dioxide on sodium thionaphthen suspended in an indifferent solvent, such as toluene, gives rise to a mixture of the sodium salts of thionaphthen-2-carboxylic and -2:3-dicarboxylic acids, which can be separated by taking advantage of the widely differing acidities or by fractionation of their esters. The latter acid has been described previously, and the former is orientated by converting it through its azide into the well-known α-hydroxythionaphthen. It appears that the product obtained by fusion with sodamide consists of about two-thirds monosodium- and one-third disodium-thionaphthen.

The following individual compounds are described: *methyl thionaphthen-2-carboxylate*, coarse prisms, m. p. 72—73°, b. p. 171°/14 mm.; *ethyl thionaphthen-2-carboxylate*, indistinct crystals, m. p. 36—37°, b. p. 181—183°/vacuum; *thionaphthen-2-carboxylic acid*, colourless, slender needles, m. p. 236° (*chloride*, colourless leaflets, m. p. 88—89°, b. p. 173—175°/19 mm.: *amide*, slender needles or leaflets, m. p. 177°; *hydrazide*, colourless, shining leaflets, m. p. 184—185°; *azide*, long, colourless needles, m. p. 108° [decomp.]): *urethane* of 2-*aminothionaphthen*, yellow crystals, m. p. 161°; 2-hydroxythionaphthen, m. p. 34—35° (the acid is not identical with that prepared by Friedländer and Link from *o*-mercaptobenzaldehyde and chloroacetic acid, which has m. p. 114°, and is designated thionaphthen-2-carboxylic acid by these authors); *methyl thionaphthen-2:3-dicarboxylate*, long, colourless prisms, m. p. 91°, b. p. 213—215°/18 mm.; thionaphthen-2:3-dicarboxylic acid, m. p. 250—251°; *thionaphthen-2:3-dicarboxylic anhydride*, pale yellow needles, m. p. 171°; *thionaphthen-2-carboxyamido-3-carboxylic acid*, $C_6H_4<\underset{S}{\overset{C(CO_2H)}{}}>C\cdot CO\cdot NH_2$, short, colourless needles, m. p. 221° (decomp.), and *thionaphthen-3-carboxyamido-2-carboxylic acid*, $C_6H_4<\underset{S}{\overset{C(CO\cdot NH_2)}{}}>C\cdot CO_2H$, short needles grouped in rosettes, m. p. 193° (decomp.), are obtained by the action of methyl-alcoholic ammonia on the

anhydride, and are separated by fractional crystallisation from glacial acetic acid. Their constitution is deduced by degrading them by Hofmann's method to the corresponding amino-acids, and warming the latter with dilute sulphuric acid, whereby they are converted into 2-hydroxythionaphthen, m. p. 34—35°, and 3-hydroxythionaphthen, m. p. 70°, respectively. *Thionaphthen-2:3-dicarboxylimide*, golden-yellow leaflets, m. p. 236—237°, is prepared by heating either of the acid amides at 200—220° until evolution of water vapour ceases, or, less advantageously, by heating the anhydride in a current of ammonia or by melting the anhydride with the calculated amount of carbamide. Degradation of the imide by Hofmann's method yields exclusively 3-hydroxythionaphthen, so that thionaphthen can readily be converted into thioindigo-red through thionaphthen-2:3-dicarboxylic acid.

H. W.

Additive Compound of Cinchonine and Cacodyl Chloride. L. C. MAILLARD and E. MURLAY (*Bull. Soc. chim.*, 1920, [iv], **27**, 756—769).—Cacodyl chloride combines directly or in chloroform solution with cinchonine to give a *compound*, $C_{19}H_{22}ON_2,Me_2AsCl$, and the crystals obtained from chloroform solution contain two molecules of the solvent. This compound is immediately decomposed by water, and cacodyl oxide is obtained. If the compound is decomposed by commercial ether, the anhydrous basic hydrochloride of cinchonine, $C_{19}H_{22}ON_2,HCl$, is obtained in a crystalline form. In the additive compound described above, the chlorine may be estimated directly by addition of nitric acid and silver nitrate.

W. G.

Proteinogenous Amines. VI. The Preparation of Histidine from Blood Corpuscle Paste. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 521—526).—The authors describe in full detail a process for the preparation of histidine from blood corpuscle paste; an average yield of 15 grams of pure histidine dichloride is obtained from 500 c.c. of the paste.

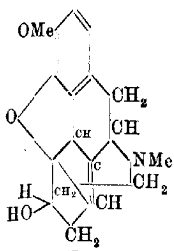
J. C. D.

Preparation of Compounds of the Morphine Alkaloids with a Derivative of Barbituric Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.-P. 322335; from *Chem. Zentr.*, 1920, iv, 392).—The alkaloids of the morphine group or their derivatives, either in the free state or as salts, are allowed to react with diallylbarbituric acid in the presence of a suitable solvent or diluent if required. The following compounds are described: *morphine–diallylbarbituric acid*, needles, m. p. 258°; *diacetylmorphine–diallylbarbituric acid*, colourless crystals, m. p. 186°; *ethylmorphine–diallylbarbituric acid*, crystalline mass; *allylmorphine sulphate*, m. p. 171°; *allylmorphine–diallylbarbituric acid*; *codeine–diallylbarbituric acid*, m. p. 105°; *dihydromorphine-*

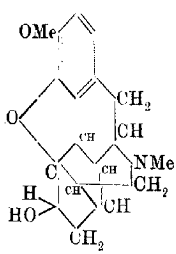
*

diallylbarbituric acid, m. p. 125°; *dihydrocodeine–diallylbarbituric acid*, m. p. 95°. H. W.

Codeine. MARTIN FREUND, W. W. MELBER, and ERICH SCHLESINGER (*J. pr. Chem.*, 1920, [ii], **101**, 1—37).—During recent years, doubts have been cast on the validity of the formula



(I.)



(II.)

(I) proposed for codeine by Knorr and his co-workers, by Gadamer and von Braun (A., 1914, i, 1138), and the alternative formula (II) has been put forward by Freund (compare Freund and Speyer A., 1916, i, 738).

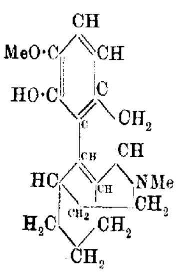
A series of attempts to gain further insight into the problem is now described; those starting from dihydrocodeine or chlorodihydrocodide did not furnish the desired information, but better results were obtained with deoxycodeine (Knorr and Waentig, A., 1917, i, 957) as initial material. This substance is reduced by sodium and alcohol to a compound, which has been described by the latter authors as dihydrodeoxycodeine, but which is now shown to be a tetrahydro-derivative; when, however, it is acted on by palladium and hydrogen, an isomeric tetrahydro-derivative is produced, the formation of which cannot be accounted for on the basis of Knorr's formula, but which is readily explained by the authors' modification thereof.

Dihydrocodeine, m. p. 86—88° (Oldenburg, D.R.-P. 260233, gives 62—63°), is unaffected by treatment with sulphuric and chromic acids under varied conditions, but is transformed by concentrated nitric acid in glacial acetic acid solution into *nitrodihydrocodeine*, yellow, crystalline powder, m. p. 221°. *Dihydrocodeine methiodide*, m. p. 257°, is readily obtained from its components, and is converted by dilute potassium hydroxide solution into *de*-N-*methyldihydrocodeine*, which could not be caused to crystallise, but which was readily converted into *de*-N-*methyldihydrocodeine methiodide*, colourless leaflets ($+\frac{1}{3}H_2O$), m. p. 173—176° (decomp.) after softening at 170° (the *perchlorate* of the base has m. p. 201—202°). *Dihydrode*-N-*methyldihydrocodeine* is obtained as a pale yellow, non-crystallisable syrup by the reduction of de-*N*-methyldihydrocodeine by hydrogen in the presence of palladium, and yields a *methiodide*, yellow powder, m. p. 219—221°, from alcohol or glacial acetic acid, colourless rods, m. p. 221—224°, from water. The methiodides evolve trimethylamine abundantly when treated with concentrated alkali hydroxide,

but the corresponding nitrogen-free bases are too readily decomposed to permit their isolation.

In the hope of obtaining better results with an analogous substance in which the hydroxyl group is not present, dihydrocodeine has been converted by phosphorus pentachloride in chloroform solution into *chlorodihydrocodide*, plates, m. p. 172—174°, which is transformed by hydrogen peroxide into *chlorodihydrocodide amino-oxide*, colourless leaflets ($+3H_2O$), m. p. 214° (decomp.), which yields the original material on treatment with sulphurous acid, and by nitric acid in hot glacial acetic acid solution is converted into a *substance*, $C_{21}H_{24}O_5N_2Cl$ [?], pale yellow, crystalline powder, m. p. 223—224°, the constitution of which was not further elucidated. *Chlorodihydrocodide methiodide*, small, colourless, matted needles, m. p. 244° (decomp.), is prepared from its components, and is converted by potassium hydroxide into *de*-N-*methylchlorodihydrocodide*, m. p. 103° after previous softening, which combines with methyl iodide to give *de*-N-*methylchlorodihydrocodide methiodide*, colourless needles, m. p. 272°; the corresponding nitrogen-free base was too unstable to permit its isolation. De-*N*-methylchlorodihydrocodide is reduced by hydrogen in the presence of palladium to *dihydrode*-N-*methylchlorodihydrocodide*, which could not be caused to crystallise, but which readily yields *dihydrode*-N-*methylchlorodihydrocodide methiodide*, colourless, slender needles decomposing at 290—291°; the latter is decomposed by boiling alkali, with evolution of trimethylamine and simultaneous decomposition of the nitrogen-free substance.

α-Chlorocodide is reduced by hydrogen in the presence of colloidal palladium to *α-dihydrodeoxycodeine*, which could not be caused to crystallise; it yields an oily *hydriodide*, *methiodide* and *perchlorate*, and a solid, but amorphous, *picrate*, *aurichloride*, and *platinichloride*.

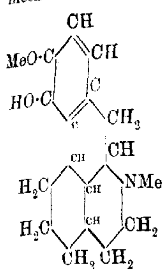


(III.)

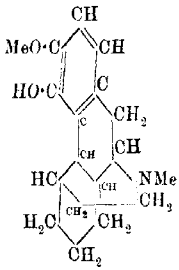
Dihydrodeoxycodeine (III), coarse, crystalline plates ($+0{\cdot}5H_2O$), m. p. 117—119°, $[\alpha]_D^{18}$ $+88{\cdot}71°$ in alcoholic solution (*hydriodide*, pale brown needles, m. p. 245°), is prepared by the electrolytic reduction of chlorodihydrocodide at a lead cathode, or in a similar manner from α- or β-chlorocodide or from deoxycodeine; the base obtained from β-chlorocodide, however, had m. p. about 126—130° after previous softening. The phenolic character of the base derived from deoxycodeine is particularly established by the isolation of the *methiodide* of the *methylated base*, long, flat needles, m. p. 245°. It would appear that deoxycodeine is not formed, as Knorr and Waentig (*loc. cit.*) suggest, by simple replacement of the hydroxyl group by hydrogen, but that it is formed by fission of the oxygen bridge.

Deoxycodeine hydrochloride is obtained by a modification of the

method of Knorr and Waentig (*loc. cit.*), and is reduced by hydrogen in aqueous solution in the presence of palladium to *β-tetrahydrodeoxycodeine* (IV); the base crystallises from methyl or ethyl alcohol in six-sided leaflets (+1 molecule of solvent), m. p. 147—148°; it is feebly lævorotatory in alcoholic solution. The *hydrochloride*, m. p. about 262° (+1EtOH), the *hydriodide*, long needles (+H_2O), m. p. 240—241°, and the *methiodide*, m. p. 263°, are described.



(IV.)



(V).

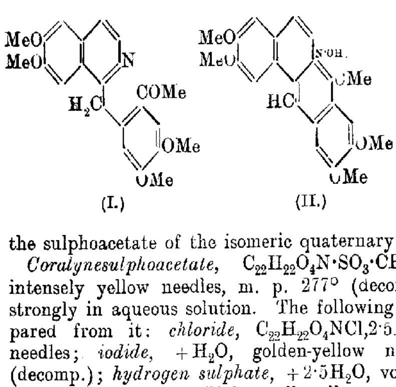
All attempts to hydrogenate the base further were unsuccessful. The *N*-methyl group could not be removed by means of cyanogen bromide. The presence of the hydroxyl group could not be established by the help of acetic anhydride, benzoyl chloride, or chloroacetyl chloride, but the base is converted by methyl sulphate and sodium hydroxide into *methoxytetrahydrodeoxycodeine*, which was identified as the *methiodide*, prisms, m. p. 255—256° after previous softening; the latter is converted by very concentrated potassium hydroxide solution into *de-N-methylmethoxytetrahydrodeoxycodeine*, pale yellow oil, which yields a *hydriodide*, small rods, m. p. about 185° after softening from 175°, and a *methiodide*, prismatic rods, m. p. 188° after softening at 185°. The action of concentrated potassium hydroxide solution on the methiodide leads to the copious evolution of trimethylamine and the formation of small quantities of a pale yellow oil, which could not be caused to crystallise. *Bromotetrahydrodeoxycodeine*,

$$C_{18}H_{24}O_2NBr,EtOH,$$

needles, m. p. about 135° (decomp.) after softening from 120°, is prepared by the interaction of bromine and the β-base in chloroform solution; the *hydrochloride*, *hydrobromide*, and *hydriodide* are viscous salts, which could not be caused to crystallise. When subjected to electrolytic reduction, the bromo-compound regenerates the parent substance. α-Tetrahydrodeoxycodeine (formula V), small leaflets or rods, m. p. 132°, is prepared by the reduction of dihydrodeoxycodeine, m. p. 117—119°, by hydrogen and palladium, or by electrolytic reduction of α-dihydrodeoxycodeine. The identity of this substance with the "deoxydihydrocodeine" obtained by Knorr and Waentig by the action of sodium and alcohol on deoxycodeine is established by its melting point and that of its hydrochloride [155° (decomp.)], and also by its conversion into α-methoxytetrahydrodeoxycodeine methiodide, m. p. 247° (Knorr and Waentig give m. p. 248—249°).

H. W.

Acetylpapaverine and Coralyne [Hexadehydrocoralydine]. WILHELM SCHNEIDER and KURT SCHROETER (*Ber.*, 1920, **53**, [*B*], 1459—1469).—Papaverine is converted by acetic anhydride, which has been previously warmed to 85° with a little concentrated sulphuric acid, into a yellow, crystalline salt, $C_{24}H_{25}O_9NS,H_2O$. The corresponding quaternary ammonium base passes in warm aqueous solution into an isomeric ketonic base, from which the original salts are regenerated by addition of acid. The phenomena are thus very similar to those observed with berberine, and, more particularly, with dehydrocorydaline (Haars, A., 1905, i, 462), from which the present compound differs in containing two atoms of hydrogen less in the molecule. The constitution of the substance is further elucidated by its conversion into *m*-hemipinic acid; it behaves in this respect in the same manner as coralydine (Pictet, A., 1913, i, 1224; 1916, i, 418), and for this reason the authors propose the name coralyne. It therefore appears that the primary product of the action of sulphoacetic anhydride on papaverine is acetylpapaverine (I), which passes by ring closure into the sulphoacetate of the isomeric quaternary coralyne base (II).



(I.) (II.)

Coralynesulphoacetate, $C_{22}H_{22}O_4N\cdot SO_3\cdot CH_2\cdot CO_2H,H_2O$, forms intensely yellow needles, m. p. 277° (decomp.), which fluoresce strongly in aqueous solution. The following salts are readily prepared from it: *chloride*, $C_{22}H_{22}O_4NCl,2\cdot5H_2O$, slender, yellow needles; *iodide*, $+H_2O$, golden-yellow needles, m. p. 278° (decomp.); *hydrogen sulphate*, $+2\cdot5H_2O$, voluminous, pale yellow precipitate; *nitrate*, $+H_2O$, small, yellow needles, which decompose above 270° without appearing to melt.

Acetylpapaverine (*ψ-coralyne*), yellowish-grey crystals, m. p. 140—141°, is readily obtained by heating a solution of coralyl sulphoacetate in water with an excess of sodium hydroxide until the solution, which originally has a dark colour, owing to the presence of the ammonium hydroxide form of coralyne, becomes pale orange; the ψ-base is stable in the dry state or when dissolved in benzene, but on contact with water or alcoholic solutions is more or less rapidly converted into the ammonium form, the rate being generally such as can be readily followed by titration with $N/10$-acid. It is interesting to note that this change is accompanied by the development of fluorescence in the solution. *Acetylpapaverineoxime* has m. p. 207°, whilst the *phenylhydrazone* forms colourless, matted needles, m. p. 208°. When treated with methyl iodide in benzene solution at 100°, acetylpapaverine gives the corresponding *methiodide*, small, pale yellow needles,

m. p. 219—220°, but in methyl-alcoholic solution it yields the quaternary coralyne iodide. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXIV. Affinity Constants and Esterification of the Pyridinecarboxylic Acids. RUDOLF WEGSCHEIDER (*Monatsh.*, 1920, **41**, 185—198).—It has been shown (this vol., i, 740) that the formation of hydrogen esters of aminodicarboxylic acids takes place, generally, in a fairly regular manner, except in the instance of the semi-hydrolysis of the normal esters, and attempts are now made to secure a more uniform conception of the esterification of the pyridinecarboxylic acids than has previously been possible. It is found that the apparently irregular affinity constants of the pyridinecarboxylic acids can be brought into line with the Ostwald factor rule in the same manner as the aromatic acids if it is assumed that these constants are influenced by internal salt formation. In general, the same factors can be used for the substituents as in the case of the aromatic acids, except for the methyl group, for which larger factors must be chosen. The formation of hydrogen esters of the pyridinecarboxylic acids in general follows the same rules as are usually valid if a steric influence is not ascribed to the nitrogen atom of the ring, and the strength of the carboxyl group is regarded as determined by a suitably modified factor rule. Exceptions are only encountered in the case of semi-hydrolysis, and this is by no means unusual.
H. W.

Manufacture of the Allyl Ester of 2-Phenylquinoline-4-carboxylic Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat., 150401).—Like the alkyl esters, the allyl ester of 2-phenylquinoline-4-carboxylic acid is tasteless, and has the further advantage of dissolving uric acid more readily than either the alkyl esters or the acid itself. It may be prepared by any of the usual methods of esterification, such as the action of an allyl haloid on a salt of the acid or by the action of allyl alcohol on the acid chloride, or on the acid itself in presence of hydrogen chloride or sulphuric acid. The ester boils at 260°/15 mm., and melts at 30°. Its hydrochloride crystallises from alcohol in small, citron-yellow needles, m. p. 145—147°, which are immediately decomposed by water. G. F. M.

Quinuclidines. JAKOB MEISENHEIMER (*Annalen*, 1920, **420**, 190—239).—The term quinuclidines has been ascribed by Koenigs (A., 1905, i, 824) to a series of bases derived from piperidine by joining the nitrogen atom to the para-carbon atom by a bridge of two carbon atoms, and the isolation of 3-ethylquinuclidine has been described. The present communication deals with the preparation of quinuclidine itself and of benzoquinuclidine according to the general method of Koenigs. The former substance has been described previously by Löffler and Stietzel (A., 1909, i, 181), but

their data differ so widely from those of the present author that it is impossible for them to have been dealing with the pure compounds. (In the following, their data are recorded in brackets after the individual substances.)

[With JULIUS NERESHEIMER and WILHELM SCHNEIDER.]—4-Pyridylethanol, colourless, viscous syrup, b. p. 151—152°/13—14 mm. (125—126°/15 mm.), is prepared by the action of formaldehyde on 4-methylpyridine, obtained by fractionation of commercial 3-methylpyridine [the method of purification by means of mercuric chloride recommended by Ahrens (A., 1905, i, 232) does not appear to be effective]; the yield is only very small, owing to the simultaneous production of di- and tri-methylol. The corresponding picrate has m. p. 134—135° (122—123°). The alcohol is converted by fuming hydriodic acid and red phosphorus into 4-*pyridylethyl iodide hydriodide*, m. p. 186—187° after darkening at about 180°, from which the corresponding picrate, slender, pale yellow needles, m. p. 114—115° (108—110°), is obtained; the latter readily decomposes in boiling aqueous or alcoholic solution, with the formation of 4-vinylpyridine picrate (see later). 4-Pyridylethyl iodide is a colourless oil, which readily decomposes spontaneously into a polymeric iodide, m. p. 267—268° (decomp.) after softening at 260° (216—218°). 4-*Pyridylethyl chloride hydrochloride*, m. p. above 260° (decomp.), is prepared from 4-pyridylethanol and fuming hydrochloric acid; the corresponding *picrate* crystallises in slender, yellow needles, m. p. 130—131°, whilst the platinichloride has m. p. 207° (decomp.) (147—148°). The free base is a colourless oil, which readily loses hydrogen chloride and forms 4-vinylpyridine in the presence of alkali hydroxide; it is transformed when gently warmed into a *polymeric quinuclidine chloride*, m. p. 255—260° (decomp.).

4-*Vinylpyridine*, almost colourless oil, b. p. 59°/12 mm. (slight decomp.), is best obtained by the action of boiling methyl-alcoholic potassium hydroxide solution on 4-pyridylethyl iodide hydriodide [the *picrate*, yellow, shining leaflets, m. p. 198—199° (decomp.) after previous softening when slowly heated, and the *platinichloride*, which softens at about 200°, but does not melt below 350°, are described]. Potassium permanganate oxidises it to a mixture of formic and *iso*nicotinic acids.

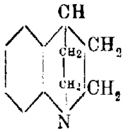
4-Piperidylethanol, almost colourless, viscous liquid, b. p. 140—141°/12—14 mm. (120—125°/15 mm.), is prepared by the reduction of 4-pyridylethanol by sodium and ethyl alcohol, and is converted by fuming hydriodic acid and red phosphorus into 4-piperidylethyl iodide hydriodide, colourless needles, m. p. 190—191° after darkening at 186° (158—159°). The latter is transformed by a slight excess of sodium hydroxide in warm aqueous solution into quinuclidine, which is conveniently isolated as the picrate, m. p. 275—276° (decomp.) after previous softening (213—215°); the free base has m. p. 158° after softening at 154° in a sealed capillary tube, and is very volatile for a substance of such high melting point. It is remarkably stable, and is scarcely

affected by concentrated sulphuric acid or nitric acid at 100°, or by potassium permanganate in sulphuric acid solution. The *platinichloride*, m. p. 238—240° (decomp.), and the *aurichloride*, large, shining leaflets, m. p. 271—273° (decomp.) after previous softening, are described. Quinuclidine unites with ethyl iodide to give the corresponding *ethiodide*, thin plates, m. p. 270—271° (slight decomp.), from which the platinichloride, leaflets, m. p. 271—272° after previous darkening (212°), is obtained.

[With OSCAR FINN and WILHELM SCHNEIDER.]—Lepidine, when heated on the boiling-water bath with 20% formaldehyde solution, yields a mixture of 4-quinolylpropanediol (picrate, m. p. 170°) and 4-quinolylethanol, prisms, m. p. 63° (picrate, m. p. 155—157°) (compare Koenigs, *loc. cit.*). The ethanol is somewhat unstable towards hydrochloric acid, which, at 100°, converts it into the dimolecular 4-vinylquinoline (see later). It is converted by hydriodic acid (D 1·96) and red phosphorus at 95° into *4-quinolylethyl iodide hydriodide*, yellow, six-sided plates, m. p. 173°; the salt is stable towards light and air when pure, but loses hydrogen iodide when its aqueous or alcoholic solution is boiled, and forms dimolecular 4-vinylquinoline. *4-Quinolylethyl iodide picrate* forms long needles, m. p. 154°. The corresponding free *base* is less stable than its salts, and loses hydrogen iodide in aqueous solution, with the formation of 4-vinylquinoline and other products. The readiest method of preparing *4-vinylquinoline* consists in boiling a solution of 4-quinolylethyl iodide hydriodide in aqueous acetone with aqueous sodium hydroxide solution; the free base is purified through the *picrate*, slender needles, m. p. 188—189°, and is thus obtained as a pale brown, viscous oil, which gradually solidifies when preserved in a desiccator, and cannot be distilled even under greatly diminished pressure, owing to the readiness with which it polymerises. It is oxidised by potassium permanganate in sulphuric acid solution to formic and 4-quinolinecarboxylic acids. The *platinichloride*, broad needles, m. p. above 275°, is described. *Bimolecular 4-vinylquinoline*, coarse crystals, m. p. 148—149°, is obtained in the pure state by evaporation of a solution of the unimolecular variety in aqueous hydrochloric acid and cautious liberation of the base by addition of alkali in the presence of ether. It is neutral towards litmus, non-volatile with steam, and cannot be distilled; it does not decolorise acid permanganate. The *hydrochloride*, m. p. between 280° and 290°, the *platinichloride*, which does not melt below 340°, and the *picrate*, thin, yellow needles, m. p. 242—243° (decomp.) after previous softening and darkening, are described. 4-Vinylquinoline picrate is transformed by boiling absolute alcohol into *4-quinolylethyl ethyl ether picrate*, broad, shining needles, m. p. 171—172° (decomp.) after marked softening at 140° when slowly heated, m. p. 140—145°, followed by resolidification and re-melting at 171—172°, when rapidly heated, the variations being due to the elimination of ethyl alcohol and formation of 4-vinylquinoline picrate, which then undergoes partial decomposition; a similar change appears to be caused by

boiling methyl alcohol, the *picrate* so obtained having m. p. 167—168° (decomp.). 4-*Quinolylethyl ethyl ether* is an almost colourless liquid, b. p. 169—170°/11—12 mm. [*platinichloride*, flat, golden-yellow prisms, m. p. 183—184° (decomp.) when rapidly heated].

Tetrahydro-4-quinolylethanol, pale yellowish-green, viscous liquid, b. p. 196—198°/11—12 mm., is prepared by the reduction of 4-quinolylethanol by sodium and ethyl alcohol; it does not yield a crystalline picrate or platinichloride, and reduces gold chloride to metallic gold. On treatment with red phosphorus and fuming hydriodic acid, the ethanol gives *tetrahydro-4-quinolylethyl iodide hydriodide* (m. p. about 100—105° in the crude condition), which is converted by aqueous sodium hydroxide solution at 60—70° into *benzoquinuclidine* (annexed formula), shining leaflets, m. p. 68—69° (*platinichloride*, yellowish-red prisms, which soften at 225° and decompose at 230°; *picrate*, slender needles, m. p. 195—196°). *Benzoquinuclidine ethiodide* forms long needles, m. p. 217—218°, and is converted by moist silver oxide into the corresponding quaternary base. H. W.



Alkylation of Pyrazolones by means of Sodium Alkyloxides. Ludwig Wolff and Ernst Thielepape (*Annalen*, 1920, **420**, 275—284).—Wolff's method for the replacement of the oxygen atom of ketones and aldehydes by hydrogen which depends on the action of sodium ethoxide on the corresponding hydrazones (A., 1912, i, 988) gives partly abnormal results when applied to pyrazolones, since alkylation is found to occur.

When 3-methylpyrazolone is heated with methyl-alcoholic sodium methoxide for fifteen hours at 220° and subsequently for nine hours at 250° it yields a mixture of butyric acid (41%) and 3:4-dimethylpyrazolone (39%), colourless crystals, m. p. 267—268°, the identity of which is established by comparison with a specimen prepared from ethyl methylacetoacetate and hydrazine hydrate; with sodium ethoxide, 3-methyl-4-ethylpyrazolone, m. p. 229°, is mainly produced, butyric acid being formed in minor quantity, whilst, with sodium propoxide, 3-methyl-4-propylpyrazolone, m. p. 206—207°, is obtained. The success of the experiment is largely dependent on the use of absolutely anhydrous alcohol, since under similar conditions, but with Kahlbaum's propyl alcohol which had not been specially treated, pyrazolylpyrazolone, m. p. 259°, was isolated in good yield. 3:4-Dimethylpyrazolone was not affected by being heated with sodium ethoxide solution during twenty-two hours at 260°. Phenylmethylpyrazolone is transformed by sodium ethoxide at 170—190° into a mixture of bisphenylmethylpyrazolone, which does not melt below 300°, and bisphenylmethylethylpyrazolone, m. p. 149—150°; more complete ethylation is effected at 220°.

3:5-Dimethylpyrazole is converted by sodium ethoxide at 250°

into a *substance*, $C_{12}H_{20}N_4$, m. p. 253° [*picrate*, m. p. 224—226° (decomp.)], which is probably tetramethylethylpyrazolylpyrazole.

H. W.

New Cases of Isomerism in the Isatin Series. IV. GUSTAV HELLER (*Ber.*, 1920, **53**, [*B*], 1545—1551. Compare A., 1917, i, 219).—Further experiments have shown that isatol has about three times the molecular weight calculated for the simple formula when dissolved in boiling glacial acetic acid or in freezing phenol or veratrole; the phenomenon is considered to be due to association rather than to polymerisation. The conversion of isatol into isatin is not a simple rearrangement, but appears to occur with intermediate formation of bimolecular isatoid-like substances. The typical properties of the isatols appear to be more clearly exhibited by dimethylisatol (the dimethylisatin, III, of A., 1918, i, 235), which is not immediately affected by alkali and is unimolecular as shown by the smooth conversion of its methyl ether into the unimolecular lactim ether when heated with glacial acetic acid; its ready conversion into a basic substance, insoluble in alkali, appears to differentiate it from methylisatoid.

The formula previously proposed for isatinone (A., 1919, i, 282) is now abandoned, since the substance is found to be identical with methylisatoid prepared by Baeyer and Oekonomides (A., 1883, 201); the name isatinol should therefore be deleted from the literature and replaced by *iso*methylisatoid. Various formulæ for these substances are considered, but a definite conclusion does not yet seem possible.

[With MARIE MEYER.]—5-Chloroisatol, m. p. 188° (decomp.), is prepared by converting chloroisatin into the silver salt and treatment of the latter with benzoyl chloride in the presence of benzene; it does not react with phenylhydrazine or with methyl sulphate at 100°, is not basic, and is converted by hot alkali into chloroisatinic acid. 5-*Chloroisatin-α*(2)-*phenylhydrazone*, slender needles, m. p. 250° (decomp.), is prepared from phenylhydrazine and chloroisatin lactim ether, m. p. about 132°, after softening at 128° in alcoholic solution; the lactim ether yields chloromethylisatoid when subjected to illumination or heated with glacial acetic acid. 5-*Bromoisatol* is prepared in the same manner as the corresponding chloro-compound. The silver salt of 5-bromoisatin is primarily converted by methyl iodide in benzene solution at 100° into 5-bromoisatin lactim ether, which is subsequently partly transformed into 5-*bromo*-N-*methylisatin*, needles, m. p. 172—173° (more conveniently prepared by the action of alcoholic sodium methoxide on 5-bromoisatin), the conversion appearing to occur more readily than with the corresponding parent substances. 5-*Bromoisatin*-2-*phenylhydrazone* forms dark red, four-sided platelets, which decompose at 241—242°.

H. W.

Azopyrazolones and Allied Compounds. KENNETH HERBERT SAUNDERS (T., 1920, **117**, 1264—1272).

Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. III. Resolution of Phenylmethylethylazonium, Phenylbenzylpropylazonium, and Phenylbenzylallylazonium Iodides into Optically Active Components. BAWA KARTAR SINGH (T., 1920, 117, 1202—1214).

Hydrazones and Azines. I. Coloured Ketazines. OTTO GERHARDT (*Monatsh.*, 1920, **41**, 199—214).—A number of ketazines have been prepared in the hope of tracing some connexion between colour and constitution in this class of substances. Even among the fluorenoneketazines, however, there seems to be no marked regularity; in spite of the presence of the chromophoric grouping, :C:N–, the close arrangement of the atoms in the molecule and the occurrence of crossed double bonds, the entrance of the auxochromic hydroxy-group in the meta-position causes only an unimportant deepening of the colour, but apparently no development of tinctorial power.

β-Hydrindoneketazine, pale pink needles, m. p. 194—195°, which undergo autoxidation on exposure to air, yielding dark red needles which could not be fully identified, is prepared by the action of hydrazine hydrate on an alcoholic solution of β-hydrindone. 2-*Nitrofluorenonehydrazone* forms dark yellow, microscopic leaflets, m. p. 214°, and is oxidised by iodine in alcoholic solution to 2-*nitrofluorenoneketazine*, brown, crystalline powder, m. p. 305—306°. 2-*Aminofluorenonehydrazone*, orange-yellow, matted needles, m. p. 201—202°, is prepared from 2-aminofluorenone and hydrazine hydrate; it cannot be oxidised by iodine to the corresponding ketazine, nor can the latter be obtained from it by the action of a further molecule of the ketone. 2-*Aceylaminofluorenone*, cinnabar-red crystals, m. p. 227—228°, is, however, readily convertible into 2-*acetylaminofluorenonehydrazone*, lemon-yellow leaflets, m. p. 212—214°, which, when treated with iodine, gives 2-*acetylaminofluorenoneketazine*, brown, crystalline powder, m. p. 303—306°; attempts to remove the acetyl groups from the latter were unsuccessful, since 2*N*-alcoholic potassium hydroxide solution was without action, whilst a saturated solution converted the substance into a viscous mass. 2-*Dimethylaminofluorenone*, dark red, crystalline powder, m. p. 146—147°, is prepared in 40% yield by the action of methyl sulphate on the aminoketone at 170—180°, and is so extensively resinified by the action of hydrazine hydrate that the corresponding hydrazone could not be isolated. 2-*Hydroxyfluorenonehydrazone*, chrome-yellow, matted needles, has m. p. 201—202°, whilst the corresponding *ketazine*, m. p. 301—303°, is a brown, crystalline powder. *Piperonaldazine*, m. p. 206—207°, crystallises in pale yellow leaflets. *Benzophenone-benzil-ketazine*, CPh_2:N·N:CPh·COPh, pale yellow crystals, m. p. 128—129°, is prepared from benzophenonehydrazone and benzil in the presence of a little alcohol at 150°, whilst *tetramethyldiaminobenzophenone-benzil-ketazine* forms orange-yellow leaflets, m. p. 173—174°.

H. W.

Ditertiary Hydrazines. XXII. Basic Tetra-arylhydrazines. HEINRICH WIELAND (*Ber.*, 1920, **53**, [*B*], 1313—1328. Compare A., 1915, i, 848, and previous abstracts).—The preparation of further substituted tetra-arylhydrazines has been attempted; the most noteworthy of the substances actually isolated is *pp'*-tetramethyldiaminodimethoxytetraphenylhydrazine,

$$(NMe_2{\cdot}C_6H_4)_2N{\cdot}N(C_6H_4{\cdot}OMe)_2,$$

in which the tendency towards dissociation is as marked as in the case of tetra-*p*-dimethylaminotetraphenylhydrazine.

[With J. SUREDA.]—pp' - *Diacetylaminotetraphenylhydrazine*, $NHAc{\cdot}C_6H_4{\cdot}NPh{\cdot}NPh{\cdot}C_6H_4{\cdot}NHAc$, colourless prisms, m. p. 124°, after slight decomposition from 100°, is obtained by the oxidation of *p*-acetylaminodiphenylamine by potassium permanganate in acetone solution; as is to be expected, the substance does not exhibit a strongly marked tendency towards dissociation, in which respect it resembles tetratolylhydrazine. Attempts to remove the acetyl groups without extensively decomposing the compound were unsuccessful.

[With E. SCHAMBERG.]—p-*Diethylaminodiphenylamine*, colourless leaflets, m. p. 88—89°, is obtained by the action of phenylhydrazine on *p*-nitrosodiethylaniline, and is converted by silver oxide in dry ethereal solution into *di* - p - *diethylaminotetraphenylhydrazine*, $NEt_2{\cdot}C_6H_4{\cdot}NPh{\cdot}NPh{\cdot}C_6H_4{\cdot}NEt_2$, m. p. 104° (darkening); in its tendency towards dissociation, the latter substance closely resembles tetra-anisylhydrazine. It is hydrolysed by water to diethylaminodiphenylamine, quinoneanil, and diethylamine. In benzene solution it readily unites with nitric oxide and triphenylmethyl to yield the *compounds*, $C_{16}H_{19}ON_3$, yellow needles, m. p. 78°, and $C_{35}H_{34}N_2$, coarse, colourless prisms, m. p. 163° (darkening), respectively.

[With FRL. E. HAAS.]—p'-*Dimethylamino*-p-*methoxydiphenylamine*, colourless leaflets, m. p. 78°, b. p. 200°/*ca.* 1 mm., is prepared by the action of *p*-iodoanisole, acetyldimethyl-*p*-phenylenediamine, potassium carbonate, copper bronze, and iodine in boiling nitrobenzene and subsequent hydrolysis of the primary product. When dissolved in a mixture of dry pyridine and ether and cooled in a freezing mixture of ice and salt, it is oxidised by silver oxide to pp'-*tetramethyldiaminodimethoxytetraphenylhydrazine*, quadratic prisms, m. p. 93°, after previous discoloration. Its solution in benzene readily absorbs nitric oxide with the formation of p'-*dimethylamino*-p-*methoxydiphenylnitrosoamine*, dark yellow leaflets, m. p. 95°.

[With E. SCHAMBERG.]—*Di*-pp'-*diethylaminodiphenylamine*, m. p. 56°, is prepared by reducing *p*-nitrosodiethylaniline with zinc dust, adding diethylaniline, oxidising with potassium dichromate, and reduction of the zinc double salt thus produced by hyposulphite. It differs from the corresponding tetramethyl base in that, as a consequence of extensive decomposition, it cannot be oxidised to the corresponding hydrazine; treatment with silver oxide in the presence of light petroleum transforms it into *diethylindophenol*, m. p. 106°.

Attempts to convert 2:4:6:2′:4′:6′-hexamethoxydiphenylamine into the corresponding hydrazine were unsuccessful. The substance is oxidised by silver oxide in acetone solution to *pentamethoxyquinoneanil*, $O:C_6H_2(OMe)_2:N\cdot C_6H_2(OMe)_3$, blackish-green, shining crystals, m. p. 202°, which is reduced by zinc dust and acetic acid to the corresponding leuco-*compound*, colourless needles, m. p. 156—157° (discoloration).

The oxidation of tetramethyldiaminodiphenylamine by an excess of silver oxide has been further studied, and the view taken previously that trimethylindamine [dimethylaminophenylmethylquinonedi-imide], $NMe:C_6H_4:N\cdot C_6H_4\cdot NMe_2$, is produced by the loss of hydrogen and methyl from the base is now abandoned, since it is found that the solution which has only been oxidised to the hydrazine stage contains only traces of the indamine. The latter owes its origin to the oxidation of the tetramethyldiaminodiphenylnitrogen radicle,

$$NMe_2\cdot C_6H_4\cdot \dot{N}\cdot C_6H_4\cdot NMe_2 \longrightarrow NMe_2\cdot C_6H_4\cdot N:C_6H_4:NMe + CH_3,$$

but the fate of the methyl radicle is not established. Isolation of trimethylindamine is most conveniently effected by treatment of the fully oxidised ethereal solution of tetramethyldiaminodiphenylamine with nitric oxide and separation of the *trimethylindaminedinitrosoamine*, yellowish-green crystals, m. p. 136° (decomp.) after softening at 130°. The latter is reduced by stannous chloride and concentrated hydrochloric acid to *trimethyldiaminodiphenylamine*, colourless needles, m. p. 73°, which is oxidised by silver oxide in the presence of ether to *trimethylindamine*, m. p. 90°; nitric oxide and triphenylmethyl are readily added by the latter. H. W.

Ditertiary Hydrazines. XXIII. Mixed Aromatic Ditertiary Hydrazines. Tetrabenzylhydrazine. HEINRICH WIELAND and EDUARD SCHAMBERG (*Ber.*, 1920, **53**, [*B*], 1329—1335).—In continuation of previous work, the authors have now examined unsymmetrical diaryldialkylhydrazines, which, in regard to their tendency towards dissociation, are found to be even more stable than the corresponding symmetrical compounds. Attempts to prepare tetra-alkylhydrazines did not meet with success, but it has been found possible to isolate tetrabenzylhydrazine, which is found to possess extraordinary stability. It appears, therefore, that the instability of the N·N linking in hydrazines is conditioned by the immediate attachment of the nitrogen atoms to aryl groups, and that the phenomenon becomes more marked when positive groups are introduced into the nucleus.

as-*Diphenyldimethylhydrazine*, large, colourless prisms, m. p. 52°, is prepared by the action of methyl sulphate on *as*-diphenylhydrazine. It is more stable than the symmetrical isomeride, and remains unchanged when boiled for hours in xylene solution. It is more sensitive towards acids than is diphenylhydrazine, since it is converted by dilute aqueous hydrochloric acid into dimethylamine, diphenylamine, and a dye, which resembles emeraldine, and, as judged from its leuco-compound, $C_{26}H_{23}N_3$, m. p.

175—176°, is composed of a molecule of diphenyldimethylhydrazine united with a molecule of diphenylamine.

Attempts to prepare tetramethylhydrazine are described, but the alkylation of hydrazomethane dihydrochloride by methyl-alcoholic sodium hydroxide solution and methyl iodide only leads to the production of N-*methyl*-N′-*trimethylhydrazonium iodide*, $NHMe{\cdot}NMe_3I$, colourless prisms, m. p. 226·5°.

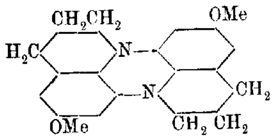
Tetrabenzylhydrazine, large, colourless prisms, m. p. 139·5°, is prepared by the action of benzyl bromide on tribenzylhydrazine. It does not yield salts. It is unaffected by protracted treatment with zinc dust and acetic acid, or by solution in concentrated sulphuric acid. When distilled under diminished pressure (260°/32 mm.), a portion passes over unchanged, whilst the remainder is decomposed into dibenzylamine and benzylbenzylideneamine. It is smoothly converted by concentrated hydrochloric acid at 160° into benzyl chloride and hydrazine.

[With FRL. E. HAAS.]—Attempts to convert di*cyclo*hexylamine into tetra*cyclo*hexylhydrazine were not successful, since a solution of the base in acetone was found to be fairly smoothly converted by permanganate into the cyclo*hexylamide* of adipic acid, $C_6H_{11}{\cdot}NH{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2H$, colourless needles, m. p. 138—139°, which was identified by hydrolysis to adipic acid and *cyclo*hexylamine.

It is shown that two diphenylamino-radicles can be very firmly united by the carbonyl group, since tetraphenylcarbamide remains unchanged when heated to 210°, and, in part, sublimes unaltered when directly distilled. H. W.

Ditertiary Hydrazines. XXIV. Ditertiary Hydrazines of the Quinoline Series. HEINRICH WIELAND and EMMY HAAS (*Ber.*, 1920, **53**, [*B*], 1336—1343).—The similarity in properties between tetrahydroquinoline and monoalkylated anilines has led the authors to attempt to obtain substances in which two quinolyl residues are united by the nitrogen bond, and thus have a formal likeness to the ditertiary hydrazines. These substances are readily obtained by the direct oxidation of tetrahydroquinoline, methyltetrahydroquinoline, and *p*-methoxytetrahydroquinoline with potassium permanganate; a similar compound could not, however, be isolated in this manner from tetrahydro*iso*quinoline. The new "quinolinehydrazines" show little tendency towards dissociation, and give colourless solutions in boiling xylene; in solvents of higher boiling point, such as ethyl benzoate, the formation of yellow or brown solutions indicates the occurrence of dissociation, but this only takes place under such conditions that the free radicles are extensively decomposed. They are not basic. They are more or less readily affected by acids. Thus, bistetrahydroquinonyl is rapidly decomposed by ethereal or aqueous (25%) hydrochloric acid, with the formation of tetrahydroquinoline and resinification of the other half of the molecule. When an ethereal solution of the hydrazine is shaken with 2*N*-hydrochloric acid, a

benzidine transformation occurs smoothly, which must be regarded as an intramolecular change without previous dissociation. In those cases in which, for constitutive reasons, a benzidine transformation is impossible, total fission occurs; the latter type of change has been most closely studied with bis-1:2:3:4-tetrahydro-6-methoxyquinonyl, which is shown to yield 6-methoxy-1 : 2 : 3 : 4 - tetrahydroquinoline (thallin) and thalloperazine (annexed formula).



The following compounds are described: *bis*-1 : 2 : 3 : 4-*tetrahydroquinolyl*, $C_9H_{10}{\cdot}N{\cdot}N{\cdot}C_9H_{10}$, large, yellow prisms, m. p. 141—142°; *tetrahydroquinobenzidine* [6:6′-*bis*-1:2:3:4-*tetrahydroquinolyl*], colourless needles, m. p. 128—129° [*dinitrosoamine*, golden rods, m. p. 196° (slight decomp.)]; N:N′-*bis*-1:2:3:4-*tetrahydro*-6-*methylquinolyl*, colourless needles, m. p. 107—108°; *thallinhydrazine*, m. p. 117—118° (slight decomp.); *thalloperazine*, yellow crystals, m. p. 160°, which, when treated with ethereal hydrogen chloride, readily yields a meriquinonoid azonium *salt*. H. W.

Some Derivatives of 4-Nitro-*o*-toluidine. Alfred Godfrey Gordon Leonard and Agnes Browne (*Sci. Proc. Roy. Dublin Soc.*, 1920, **16** [N.S.], 105—108).—When *p*-nitro-*o*-toluidine sulphate was diazotised in aqueous suspension and added to a cold alkaline solution of β-naphthol, 5-nitro-*o*-tolueneazo-β-naphthol, m. p. 204°, was obtained, which dyed cotton a deep orange colour. When the nitrotoluidine was diazotised and added to *o*-toluidine hydrochloride, 5-*nitro*-o-*toluenediazoamino*-o-*toluene*, m. p. 133°, was obtained. 5-*Nitro*-o-*toluenediazoamino*-p-*toluene*, m. p. 131° (decomp.), 5-*nitro*-o-*toluenediazoaminobenzene*-p-*sulphonic acid*, m. p. 129° (decomp.); 5-*nitro*-o-*toluenediazoamino*-p-*nitrobenzene*, m. p. 118° (decomp.), and p-*nitro*-o-*tolueneazoresorcinol*, m. p. 234°, were obtained in a similar manner. W. G.

O. Fischer's Bases from *p*-Nitrosoanilines and Arylhydrazines. Arylazohydroxyanilides [Aryldiazohydroxylaminobenzenes]. Eugen Bamberger (*Annalen*, 1920, 420, 137—169).—O. Fischer and Hepp (A., 1888, 460) have described a peculiar class of substances obtained from *p*-nitrosoaniline, *p*-nitrosomonomethylaniline, and *p*-nitrosodimethylaniline on the one hand, and phenylhydrazine, α-methylphenylhydrazine, and diphenylhydrazine on the other, which they have termed diazobenzenenitrosoanilines (compare Fischer and Wacker, A., 1888, 1286; 1889, 702). Recently, Fischer and Johannes (A., 1915, i, 907) have pointed out that these compounds are simply the *p*-amino-substitution products of the diazoxyaminobenzenes obtained by Bamberger (A., 1918, i, 20; 1899, i, 589) by the con-

densation of diazonium salts with β-phenylhydroxylamine, and are best represented by one of the following formulæ:

$$NR_2\cdot C_6H_4\cdot NO\colon N\cdot NPhR'$$

or $NR_2\cdot C_6H_4\cdot N\overset{O}{\diagup\!\!\!-\!\!\!\diagdown} N\cdot NPhR'$. The latter substances are obtained also from nitrosobenzenes and phenylhydrazines, and the formation of Fischer's bases is probably represented by the equations

$$2NH_2\cdot C_6H_4\cdot NO + 2H_2N\cdot NHPh = 2[H_2N\cdot C_6H_4\cdot N(OH)\cdot NH\cdot NHPh] = 2NH_2\cdot C_6H_4\cdot N(OH)\cdot N\colon NPh + 2H_2$$

and $H_2N\cdot C_6H_4\cdot NO + 2H_2 = C_6H_4(NH_2)_2 + H_2O$. Substituted and unsubstituted nitrosoaryls yield arylazohydroxyanilides [diazohydroxylaminobenzenes] with primary arylhydrazines and arylazoanilide oxides with secondary hydrazines.

[With ALEXANDER LANDAU, K. BLASKOPF, E. HINDERMANN, and H. BÜSDORF.]—Benzenediazohydroxylamino-p-dimethylaminobenzene, $NMe_2\cdot C_6H_4\cdot N(OH)\cdot N\colon NPh$ (Fischer and Wacker, *loc. cit.*), decomposes at different temperatures, 113° or 119°, according to the rate of heating (the *copper* salt is described); attempts to methylate it with methyl sulphate and potassium hydroxide led to the formation of tetramethyldiaminoazobenzene, and, possibly, a small amount of the desired ether, m. p. 135—142° (decomp.). Benzenediazohydroxylamino-p-aminobenzene yields a bluish-green *copper* salt, decomposing with explosion at 186—187°, and, when pure, yields colourless salts with acids; with potassium ethoxide solution, a yellow *potassium* salt is produced, which is hydrolysed by water.

Diazohydroxylaminobenzene is rapidly decomposed by boiling concentrated hydrochloric acid into nitrogen, phenol, and p-chloroaniline. When treated with potassium ethoxide and methyl sulphate, it yields acetaldehyde, benzene, and azobenzene, whilst the latter is also obtained when methyl iodide is used; it is unaffected by diazomethane. Zinc dust and acetic acid reduce it to aniline and phenylhydrazine. The presence of the hydroxyl group cannot be established by means of sulphur dioxide (as in the case of phenylhydroxylamine), since aniline and benzenediazonium sulphate are formed. p-Toluenediazohydroxylaminobenzene is similarly reduced to aniline and p-toluenediazonium sulphate.

p-*Nitrobenzenediazohydroxylaminobenzene*, from diazotised p-nitroaniline and phenylhydroxylamine, forms slender, pale yellow needles, which decompose at 175°, or at 185° when placed in a bath pre-heated to 174°; the *potassium* and *sodium* salts are described. Attempts to prepare the methyl ether were not successful, the sole product isolated being p-iodonitrobenzene.

The decomposition of isomeric aryldiazohydroxylaminobenzenes, $R\cdot N_2\cdot N(OH)R'$ and $R'\cdot N_2\cdot N(OH)R$, by mineral acids has been investigated in a number of cases. p-*Tolueneazohydroxylaminobenzene*, sulphur-yellow needles, which rapidly become brown on

exposure to sunlight, m. p. 130—131° (decomp.), is converted by sulphuric acid into nitrogen, *p*-cresol, and phenylhydroxylamine (or *p*-aminophenol), whilst benzenediazohydroxylamino-*p*-toluene, m. p. 123·5—124°, yields nitrogen, phenol, and *p*-tolylhydroxylamine (or toluquinol). Similarly, *benzenediazohydroxylamino*-p-*bromobenzene*, golden needles, grouped in clusters, m. p. 128·5°, gives nitrogen, phenol, *p*-dibromoazoxybenzene, and *p*-bromoaniline (the latter two being derived from *p*-bromophenylhydroxylamine), whilst *p*-bromobenzenediazohydroxylaminobenzene, straw-yellow needles, m. p. 154·5°, is decomposed into nitrogen, *p*-bromophenol, and phenylhydroxylamine. p-*Toluenediazohydroxylamino*-p-*bromobenzene*, greenish-yellow, matted needles, decomposing at 122—123° when slowly heated, but at 134° when placed in a bath pre-heated to 100°, is transformed by dilute hydrochloric acid into *p*-cresol, *pp'*-dibromoazoxybenzene, *o*-chloro-*p*-bromoaniline, and *p*-bromoaniline (the three substances last named being derived from *p*-bromophenylhydroxylamine), whereas p-*bromobenzenediazohydroxylamino*-p-*toluene*, greenish-yellow needles, which decompose at 151°, is decomposed by boiling dilute sulphuric acid into nitrogen, toluquinol, and *p*-toluidine.

Fuller details are given with regard to the action of phenylhydrazine on nitrosoaryls. In general, the substances are mixed in alcoholic solution at 0°, when action occurs with greater or less rapidity, accompanied by slight, but persistent, evolution of gas. In this manner, nitrosobenzene and phenylhydrazine yield diazohydroxylaminobenzene, phenylhydroxylamine, and, probably, azobenzene. *p*-Tolylhydrazine gives *p*-toluenediazohydroxylaminobenzene and phenylhydroxylamine, whilst the isomeric anilide and *p*-tolylhydroxylamine are obtained from *p*-nitrosotoluene and phenylhydrazine. *p*-Bromonitrosobenzene and phenylhydrazine yield benzenediazohydroxylamino-*p*-bromobenzene and *p*-bromophenylhydroxylamine (or *pp'*-dibromoazoxybenzene and *p*-bromoaniline). H. W.

Does Gliadin contain Amide Nitrogen? THOMAS B. OSBORNE and OWEN L. NOLAN (*J. Biol. Chem.*, 1920, **43**, 311—316).—Boiling gliadin with 1% hydrochloric acid for two hours yields almost as much ammonia as boiling for twenty-four hours with 20% acid. The slight increase in free amino-nitrogen after boiling with the dilute acid shows that a very slight hydrolysis of peptide linkings occurs. Since upwards of 90% of the ammonia is yielded at a rate strictly proportional to the time of boiling, as well as the concentration of the acid, it seems fair to assume that nearly all the ammonia originates from a common group, which, like $R-CO\cdot NH_2$, is very readily hydrolysed.

There is also an increase in acidity during the mild hydrolysis which corresponds with carboxyl groups nearly, if not quite, equivalent to the ammonia produced.

The uramino-group would appear to be present in extremely small amounts, if at all, in gliadin. J. C. D.

Oxygen-capacity of Hæmoglobin. R. WERTHEIMER (*Biochem. Zeitsch.*, 1920, **106**, 12—22).—Measurements made by means of a Barcroft's differential apparatus show that, in a solution rendered alkaline by addition of sodium carbonate, 1 gram of hæmoglobin fixes at the ordinary temperature and under medium atmospheric pressure 1·33 c.c. of oxygen, which is almost the exact quantity required by Hüfner's assumption that the hæmoglobin and oxygen combine in molecular proportions (A., 1893, i, 616). With a pure, aqueous solution of hæmoglobin, the proportion of oxygen combined is about 7% less than that given above.

T. H. P.

A New Hæmatin-like Crystalline Substance. S. PARTOS (*Biochem. Zeitsch.*, 1920, **105**, 49—59).—By heating defibrinated blood containing 1% of sodium sulphate, pressing the coagulum, washing it with hot water, again pressing it, and extracting with 92% methyl alcohol containing 3% of formic acid, the author has obtained a substance crystallising mostly in short needles. In some of its characters, this substance agrees with hæmatin, but it contains only 7·41—8·00% of iron, whereas hæmatin contains 8·9%; furthermore, the maxima of light-absorption in the two cases do not correspond.

T. H. P.

Calorimetric Investigations on Melanins. II. FRANZ VON HOEFFT (*Biochem. Zeitsch.*, 1920, **106**, 207—211).—Further observations are described supplementing those previously made (this vol., i, 686).

T. H. P.

Hydrolysis of Nucleotides. M. YAMAGAWA (*J. Biol. Chem.*, 1920, **43**, 339—353).—Early in the work on nucleotides, it was observed that these compounds differed from one another in their resistance to hydrolysis.

Since it is possible that the nucleotides differ in the position at which the phosphoric acid radicle is attached to the carbohydrate group, it was decided to compare the rates of hydrolysis of a number of these compounds (compare this vol., i, 712). In only one compound of this type, inosic acid, is the position of the phosphoric acid known, namely, linked to the fifth carbon atom. The rates of hydrolysis by $0{\cdot}1N$-sulphuric acid at 100° in a sealed tube were studied. The unimolecular law was followed, and the following constants, K, were obtained:

	K.
Nucleic acid	130 (10^{-2})
Guanosinephosphoric acid	177 (10^{-2})
Adenosinephosphoric acid	166 (10^{-2})
Uridinephosphoric acid	480 (10^{-3})
Inosic acid	470 (10^{-3})
Hexathymidinediphosphoric acid	726 (10^{-3})

Thus the velocity-constants of the guanosinephosphoric and the adenosinephosphoric acids are identical. On the other hand, the constants of inosic and uridinephosphoric acids are also identical,

in spite of the fact that their basic component is of a different nature. J. C. D.

Structure of Yeast-nucleic Acid. Ammonia Hydrolysis: the so-called Trinucleotide of Thannhauser and Dorfmüller. P. A. LEVENE (*J. Biol Chem.*, 1920, **43**, 379—382).—A previous communication (this vol., i, 193) has dealt with the theoretical arguments against the conception of the structure of yeast-nucleic acid suggested by Thannhauser and Dorfmüller (A., 1918, i, 47). In order to support these criticisms with evidence obtained from actual experiment, the author has shown that the conditions of hydrolysis employed by Thannhauser and Dorfmüller are such as to produce a mixture of mononucleotides, and not a trinucleotide. J. C. D.

The Occurrence of Optical Antipodes in Nature. HANS PRINGSHEIM (*Ber.*, 1920, **53**, [*B*], 1372—1374).—In a recent communication, Hess and Weltzien (this vol., i, 328) have adduced arguments which lead them to the conclusion that a fundamental difference exists between chemical processes in the vegetable and animal kingdoms, and that whereas the animal organism only builds and degrades asymmetrically, and hence involves enzymes of asymmetric structure, the vegetable organism can also build symmetrically, and hence involve symmetrical enzymes. The author considers this statement to be too general, and points out that racemic substances are also formed, if exceptionally, in the animal organism, and cites, as example, the occurrence of *dl*-arabinose in certain urines. On broader grounds, he considers that the specific action of an enzyme is only conditional, and that whilst a ferment preferentially attacks one modification of a given compound, it can, in case of necessity, also attack the antipode. So rigid a classification of symmetrical and asymmetrical ferments does not appear to have been attempted previously, and until more is known of the chemical structure of ferments, it appears too early to assume that steric arrangements must of necessity be present in them as in the substrates. H. W.

The Ability of Plants to Form Optical Antipodes. KURT HESS (*Ber.*, 1920, **53**, [*B*], 1375—1378. Compare Hess and Weltzien, this vol., i, 328).—A reply to Pringsheim (preceding abstract). Although noting that exceptions to Fischer's rule are much more common among plants and the lower organisms than among animals, the author admits that his suggestion of a "fundamental difference between the vegetable and the animal organism" is possibly too general. He considers, however, that there is abundant evidence of the asymmetric molecular structure of enzymes, and supports his contention by arguments based on the work of van't Hoff, E. Fischer, Bredig, Rosenthaler, and Bourquelot and Bridel. H. W.

The Chemical Nature of Enzymes. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, **100**, 100—113).—The alkylamino-nitrogen was

estimated in a number of well-known enzymes by means of nitrous acid. The amino-nitrogen was found to vary from 3·05% in rennet to 7·66% in papayotin. The author considers that the results obtained are in favour of the theory of the protein nature of enzymes. S. S. Z.

Destruction of Rennet and Pepsin by Alkali. L. MICHAELIS and M. ROTHSTEIN (*Biochem. Zeitsch.*, 1920, **105**, 60—87).—The method used to arrive at a quantitative measure of these two enzymes consists in determining by trial that dilution of the enzyme solution which corresponds in its activity with a control solution prepared so as to be readily reproducible. The action was measured by means of the coagulation of milk containing calcium chloride in the case of rennet, and by the gradual clearing of an albumin solution rendered turbid by addition of sulphosalicylic acid in the case of pepsin.

If the hydrogen-ion concentration of a rennet solution is adjusted by means of a mixture of phosphates, the enzyme remains practically unrestricted with an acid reaction down to $p_H = 6$. As neutrality is approached, a rapid destruction of the enzyme suddenly begins, the velocity of the destruction quickly becoming immeasurably great as the value of p_H diminishes further. For a given value of p_H, the destruction of rennet is not a unimolecular reaction, the velocity of the destruction at any moment being proportional to the 1·5th power of the amount of enzyme still present; the course of the destruction is not influenced by the enzyme already destroyed. For a given quantity of enzyme, the velocity of the destruction is proportional inversely to the fourth power of the $H^{\cdot}$-concentration, or directly to the fourth power of the OH'-concentration.

As regards the velocities of destruction at different temperatures (25·5° and 36·8°), these are identical if the solutions compared are of equal concentrations of hydroxyl ions, that is, the "physical" temperature-coefficient of the velocity is practically zero. When, however, the concentration of the hydrogen ions is the same in the two solutions, the velocity of destruction at 36·8° is thirty-one times that at 25·5°, so that the "physiological" temperature-coefficient is of considerable magnitude. From the purely physical point of view, the former method of formulation is the more correct, since the hydroxyl ions represent the destroying agency; the other method is, however, of the greater physiological importance, because in the fluids of the body the concentration of the hydrogen ions, but not that of the hydroxyl ions, is almost independent of the temperature.

Destruction of pepsin by hydroxyl ions always proceeds proportionally to that of rennet, no disproportionality being observable, even after partial adsorption of the enzyme solution by kaolin. The kinetics of the reaction is expressed empirically by the equation $-dx/dt = k \cdot x^{\frac{3}{2}} \cdot [OH']^4$, where x represents the quantity of enzyme present at time t. T. H. P.

The Influence of Neutral Alkali Salts on Diastatic Enzymes. I. AMANDUS HAHN and KARL HARPUDER (*Zeitsch. Biol.*, 1920, **71**, 287—301).—The optimum H-ion concentration for the activity of ptyalin is $p_H = 6\cdot4$—$6\cdot5$, and for that of malt diastase $p_H = 4\cdot7$. The enzymic activity is not only influenced by the H-ion concentration of the buffers, but by the concentration of the other ions contained in them. The combination of neutral alkali salts with the buffers produces either an accelerating or inhibiting influence, according to the reaction and concentration of the salts and buffers, on the activity of the enzymes. The optimum H-ion concentration is also changed by the combined influence of the neutral salts and the buffers. S. S. Z.

The Influence of Neutral Alkali Salts on Diastatic Enzymes. II. AMANDUS HAHN and KARL HARPUDER (*Zeitsch. Biol.*, 1920, **71**, 302—310).—Neutral alkali salts move the isoelectric point of ptyalin and malt diastase in the acid direction. The influence of sodium salts in this respect is more marked than that of potassium salts. The mode of action of the above enzymes is independent of their electrical nature. S. S. Z.

The Process of Purifying Pancreatic Amylase. H. C. SHERMAN, I. D. GARARD, and V. K. LAMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1900—1907).—A further study of the process of purification of pancreatic amylase previously described (compare A., 1911, i, 827), a determination of the total solids and enzyme activity being made at each stage. It was found that alcohol up to 5%, or an alcohol-ether mixture up to 8%, of the volume of the substrate did not materially affect the activity of the pancreatic amylase. When extracts of pancreatin in 50% alcohol were precipitated by an alcohol-ether mixture, the residual solution contained about 1% of the active amylase and 2·5% of the solids of the original pancreatin, or about 5% of the solids originally extracted. When this precipitate was dispersed in water and mixed with alcohol, the filtrate showed no amylolytic activity, although it contained 25% of the solids originally extracted. In the process of purification used, about 50% of the amylolytic activity was lost by the end of the dialysis, but by using liquid-air cooling, it was possible in other experiments considerably to increase the proportion of active amylase recovered in the final product. The precipitate ("sac precipitate") which formed in the inner solution during dialysis showed very high proteolytic and little or no amylolytic activity. W. G.

Influence of Neutral Salts on Ferment Action. S. M. NEUSCHLOSZ (*Pflüger's Archiv*, 1920, **181**, 45—64; from *Chem. Zentr.*, 1920, iii, 355. Compare this vol., i, 698).—Investigation of the influence of neutral salts, singly and in conjunction, on the fission of sucrose by invertase on the one hand and on the surface tension of invertase solutions on the other, leads to the conclusion that the restrictive action of neutral salts on fermentative activity depends on a diminution of the dispersivity and of

the active surface of the ferment. The antagonism of ionic actions towards fermentation is shown in the diminution of the coefficient, K, of the adsorption isotherm for the action of cations in mixtures of salts; when the antagonism is maximal, this has its minimal value. H. W.

Decomposition of Tyrosinase into Components. HUGO HAEHN (*Biochem. Zeitsch.*, 1920, **105**, 169—192).—Further experiments have been made in order to ascertain to what salts the activating effect of the ash of the ultra-filtrate on α-tyrosinase is due (compare this vol., i, 102).

The action of tyrosinase proceeds best when the reaction of the solution is approximately neutral, hydroxyl ions and the hydrogen ions of acetic, lactic, and hydrochloric acids exerting a retarding influence. Salts of a number of metals have been investigated, and it is found that zinc, cadmium, and calcium ions cause the most marked activation of α-tyrosinase, and surpass in their action the ash of the ultra-filtrate itself. The phosphoric anion also strongly activates α-tyrosinase. The latter is an organic substance which undergoes decomposition only at 80°, and is not decomposed by proteolytic enzymes.

Tyrosinase must be regarded as a mixture of enzymes. According to various investigators, the tyrosine is first decomposed by means of the aminoacidase in the sense of Strecker's equation, the phenolase then introducing a hydroxyl into the benzene nucleus. Subsequently, the melanin molecule is developed by the action of condensing enzymes, these being activated by metallic salts. It is to such salts that melanin owes its characteristic coloration.

T. H. P.

Organic Compounds of Arsenic. I. Reaction between the Grignard Reagent and Arsenious Chloride. KAORU MATSUMIYA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 217—223).—When arsenious chloride acts on magnesium phenyl bromide in ethereal solution in equimolecular proportions, the product is triphenylarsine if the former is added gradually to the latter. If, however, magnesium phenyl bromide is added to arsenious chloride, the product is diphenylchloroarsine. Under similar conditions, magnesium α-naphthyl bromide gives *tri-α-naphthylarsine*, m. p. 248°, and *di-α-naphthylchloroarsine*, m. p. 116—117°, respectively.

W. G.

The Theory of Electrolytic Ions. XVII. The Conductivity of the Sodium Arsinates. RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, **112**, 209—220).—The conductivities of the sodium salts of a number of substituted phenylarsinic acids have been measured at dilutions from 23 to 1024, and the limiting conductivities at infinite dilution have been calculated from the two Kohlrausch extrapolation formulæ, $\mu_{\infty} - \mu = a[S_0]^{\frac{1}{2}}$ and $\mu_{\infty} - \mu = b[S_0]^{\frac{1}{3}}$ (compare this vol., ii, 6). The smallest conductivities were shown by the neutral monosodium salts of amino-substituted acids, for example, sodium arsanilate,

o-aminotolylarsinate, *oo'*-diaminodiphenylarsinate, and dimethyl-aminophenylarsinate, the mono-acid salts of bivalent acids, such as dichloro- and dibromo-hydroxyphenylarsinic, *m*-dihydroxyphenyl-arsinic, and the di-acid salt of 3-nitro-4-hydroxyphenylarsinic acid ($\mu_\infty = 75$—100). A second group, $\mu_\infty = 100$—200, comprised the neutral salts of bivalent acids, such as those mentioned above and the mono-acid salts of tribasic acids. Higher conductivities were shown by the neutral salts of the tribasic acids, 3-nitro-4-hydroxy-phenylarsinic acid (329) and dinitrohydroxyphenylarsinic acid (330), by the mono-acid salt of phenylene-1:4-diarsinic acid (287), and the neutral salt of the same acid (392). The aminophenyl-arsinic acids are probably monobasic through internal ring formation between the amino-group and the arsinic acid residue.

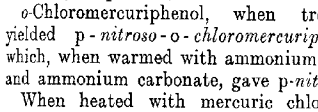
E. H. R.

Compounds of Arsenic Acid and Catechol. II. R. F. WEINLAND and J. HEINZLER (*Ber.*, 1920, **53**, [*B*], 1358—1368).—The authors have described previously the preparation of catechol semiarsenate, $AsO(O\cdot C_6H_4\cdot OH)_3,4H_2O$, and certain of its salts (A., 1919, i, 442); additional compounds of the acid are now discussed.

Catechol semiarsenate forms rhombic bipyramidal crystals, $a:b:c = 0.958:1:0.988$ (the *dihydrate*, dimethyl alcoholate, colourless rods, and diethyl alcoholate, long, colourless, flat prisms, are described); the free acid is hydrolysed by water, about 36% of the substance being present unchanged in 5% aqueous solution. The following salts are described, in which (as in the previous examples) the acid is monobasic unless the contrary is specifically stated: *lithium* salt ($+4H_2O$), shining, stout, four-sided plates; *mercurous* salt, $\left[AsO(O\cdot C_6H_4\cdot O)_3\right]\begin{matrix}Hg_2\\H\end{matrix}$, dark brown, crystalline powder, which becomes yellowish-brown on exposure to air, owing to the absorption of about 1% of water; *thallium* salt, ice-like crystals; *chromium* salt ($+12H_2O$), greenish-black cubes; *aluminium* salt ($+12H_2O$), cubes; *cerium* salt ($+15H_2O$), colourless needles; *lanthanum* salt ($+15H_2O$), colourless needles; *yttrium* salt ($+15H_2O$), colourless needles; *hexamminecobalti*-salt, $\left[AsO(O\cdot C_6H_4\cdot O)_3\right]_3\begin{matrix}Co(NH_3)_6\\H_6\end{matrix}$, four-sided, yellowish-brown leaflets; *aquopentamminecobalti*-salt, acute, four-sided, brownish-red leaflets; *chloropentamminecobalti*-salt, short, copper-red rodlets; *aquopentamminenickeli*-salt, rhombic, lilac platelets; *monopyridine* salt, colourless, crystalline powder; *dipyridine* salt, stout, well-formed prisms, which continuously evolve pyridine; *monoquinoline* salt, yellowish-white powder (the salt is so sparingly soluble that, under definite conditions, it can be utilised in the gravimetric estimation of quinoline); *salt* with 1·5 molecules of quinoline, yellow, pointed rods; *monoaniline* salt, rods or pyramids; *dianiline* salt, stout, rectangular plates or rods; *guanidine* salt, colourless crystals resembling magnesium ammonium phosphate.

As is to be expected from its behaviour with pyridine and quinoline, catechol semiarsenate yields sparingly soluble salts with the alkaloids; this has been demonstrated in the cases of morphine, quinine, strychnine, colchicine, hydrastinine, veratrine, coniine, and *apo*morphine. H. W.

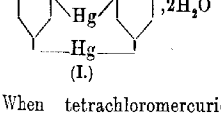
Aromatic Mercuri-organic Derivatives. MORRIS S. KHARASCH and JEAN F. PICCARD (*J. Amer. Chem. Soc.*, 1920, **42**, 1855—1864).—Methods are outlined for the preparation of a six-atom heterocyclic ring containing mercury in place of a non-metal. By the action of methyl sulphate on *m*-bromoaniline in the presence of sodium carbonate, a mixture of *m*-bromomethylaniline and *m*-bromodimethylaniline was obtained, from which, by treatment with sodium nitrite and hydrochloric acid, *m*-bromo-*p*-nitrosodimethylaniline and m-*bromophenylmethylnitrosoamine*, m. p. 49°, were obtained. By reduction with stannous chloride and hydrochloric acid, *m*-bromo-*p*-nitrosodimethylaniline yielded m-*bromodimethyl*-p-*phenylenediamine dihydrochloride*, giving the free *base*, m. p. 47·5°. The free base, when mixed with *m*-bromodimethylaniline and the mixture oxidised with potassium dichromate in hydrochloric acid solution, gave, on the addition of zinc chloride, oo′-*dibromo-Bindschedler's green*, $C_{32}H_{36}N_6Br_4Cl_2,ZnCl_2$, from which, by addition of mercuric chloride, the double *mercuric chloride* salt (annexed formula) was obtained.



m-Bromophenylmethylnitrosoamine, when dissolved in a mixture of ether and alcohol and the solution saturated with hydrogen chloride, underwent molecular rearrangement, giving m-*bromo*-p-*nitrosomethylaniline hydrochloride*, m. p. 168°, from which the free *base* was obtained.

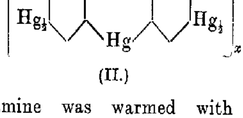
o-Chloromercuriphenol, when treated with nitrous acid, yielded p-*nitroso*-o-*chloromercuriphenol*, $OH\cdot C_6H_3(NO)\cdot HgCl$, which, when warmed with ammonium chloride, ammonium acetate, and ammonium carbonate, gave p-*nitroso-o-chloromercurianiline*.

When heated with mercuric chloride, diphenylamine yielded *tetrachloromercuridiphenylamine*, $NH[C_6H_3(HgCl)_2]_2$, from which, by the action of sodium thiosulphate, 3 : 3′-*mercurimercazine* (formula I or II) was obtained.



(I.)

or



(II.)

When tetrachloromercuridiphenylamine was warmed with a mixture of sulphuric and nitric acids, *dinitro*-2 : 2′ : 3-*trichloromercuridiphenylamine* was obtained, which, by the action of sodium thiosulphate, yielded *mercury-bis-3-dinitro*(?)-*mercazine*. W. G.

Mercuration. V. Mercuration of Phenol Ethers. W. MANCHOT and F. BÖSSENECKER (*Annalen*, 1920, **421**, 331—345).—Volhard and Dimroth have shown that the mercuration of derivatives of benzene occurs in such a manner that a hydrogen atom attached to the ring is replaced by the group HgX. The authors' work on the mercuration of ethylene and its derivatives has, however, rendered it not improbable that the primary products are additive compounds. Experiments with various phenol ethers tend to show that such is actually the case. The products obtained with mercuric acetate vary with the particular ether used, but may be classified as more or less completely hydrolysed additive compounds. They are readily decomposed by treatment with warm dilute hydrochloric acid, and are immediately converted by alkali haloids into products which are mercurated in the nucleus.

p-Tolyl methyl ether slowly reacts with aqueous mercuric acetate solution at 50°, giving the *substance*,

$$3C_6H_4Me\cdot OMe\cdot Hg(C_2H_3O_2)_2,2HgO,$$

thin, colourless needles, m. p. 132—133°, immediately transformed by sodium chloride solution into the *product*, $C_6H_3Me\cdot OMe\cdot HgCl$, colourless needles, m. p. 162°. Similarly, anisole yields the *compound*, $C_7H_8O,Hg(OH)_2$, slender needles, m. p. 173°, which forms anisole when treated with dilute hydrochloric acid, and *p*-anisylmercuri-chloride, m. p. 236—237°, under the action of sodium chloride. In like manner, phenetole gives the *substance*,

$$OEt\cdot C_6H_5,Hg(OH)_2,$$

small, matted needles, m. p. 135·5°, which is converted by potassium bromide into *p*-phenetylmercuri-bromide, needles, m. p. 238°. H. W.

Physiological Chemistry.

Hydrogen-ion Measurements on Blood in the Neighbourhood of the Isoelectric Point of Hæmoglobin. T. R. PARSONS and WINIFRED PARSONS (*Proc. Physiol. Soc.*, *J. Physiol.*, 1920, **53**, c—cii).—The view having been elaborated that, under physiological conditions, hæmoglobin is an acid of sufficient strength to expel carbon dioxide from sodium hydrogen carbonate at low tensions of the gas, it became of interest to observe the changes in its acid properties as the reaction of the medium in which it occurs approaches the isoelectric point. There is a sudden increase in carbon dioxide combining power in completely reduced hæmolysed blood, similar to that noted by Straub and Meier (A., 1918, ii, 467; 1919, i, 53) in acidified oxygenated whole and hæmolysed blood at a certain hydrogen-ion concentration not far removed from neutral point.

Hydrogen-ion measurements were made at various tensions of carbon dioxide, and these results show that over a certain range, depending on the exact amount of lactic acid present, the hydrogen

ion of the hæmolysed blood remains constant. It therefore appears that during this sudden increase of carbon dioxide combining power near the neutral point, the extra carbon dioxide is taken up in the form of sodium carbonate, and does not combine directly with hæmoglobin.

The reason why one molecule of extra carbon dioxide corresponds with each molecule of hæmoglobin seems to be that each hæmoglobin molecule is parting with one atom of available sodium for the formation of bicarbonate. It should be noted that this region of constant hydrogen-ion concentration is still on the alkaline side of the isoelectric point of hæmoglobin. J. C. D.

Occurrence of Creatinine and Creatine in the Blood in Healthy and Pathological Cases. IV. Revision of Previous Methods and Results. JOH. FEIGL (*Biochem. Zeitsch.*, 1920, **105**, 255—281. Compare A., 1918, i, 202, 357).—The considerations here presented show that the numbers obtained by Folin's older method for the proportion of pre-formed creatinine in the blood are to be regarded as trustworthy, but that the results obtained by American and German investigators for creatine are valueless. Revised procedure is described, and new results given for blood of healthy and diseased subjects. T. H. P.

The Appearance of Aldehyde-like Substances in the Blood of Six Persons (Diabetes Mellitus, Diseases of the Kidneys). WILHELM STEPP (*Biochem. Zeitsch.*, 1920, **107**, 60—80).—The presence of substances possessing the properties of aldehydes was established in the blood of some diabetic, nephritic, and other patients. These substances form iodoform with iodine in alkaline solution, and reduce Fehling's solution as well as ammoniacal silver, and give a red coloration with magenta-sulphurous acid. They are destroyed on being heated with silver oxide. In certain cases, the Rimini reaction was also obtained. The above reactions were also obtained from distillates in alkaline solution. S. S. Z.

Physiology of Blood Sugar. III. The Residual Reduction of Blood. RICH. EGE (*Biochem. Zeitsch.*, 1920, **107**, 229—245. Compare A., 1918, i, 356; ii, 278).—The residual reducing capacity of blood can be estimated by fermenting the reducing sugars with yeast. The reducing capacity of the yeast, as well as its activity, must be taken into consideration. The residual reduction of blood as estimated by Bang's micro-method is extremely small, and is of the same order in the plasma as in the corpuscles. Arterial and venous blood also show the same residual reduction. S. S. Z.

The Chemistry of the Blood-colouring Substances. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **100**, 64—80).—According to the authors, there is only one substance, *haemochrome*, which is responsible for the colour of blood. It is an amorphous powder, which exists in colloidal solution in water. In alcohol and bicarbonate, on the other hand, it exists in real

solution. The spectroscopic behaviour of hæmochrome is influenced by the solvent in which it is dissolved. Hæmoglobin is hæmochrome adsorbed by globin. S. S. Z.

The Biochemistry of Phosphatides and Sterols. I R. Brinkman and (Frl.) E. van Dam (*Biochem. Zeitsch.*, 1920, **108**, 35—51).—The osmotic resistance of blood corpuscles raised by washing them with a physiological salt solution (0·85% NaCl) is due to the removal of the adhering lecithin, which is adsorbed by them from the plasma, and which is responsible for lowering their osmotic resistance. Cholesterol has the opposite effect. An isotonic sucrose solution does not remove the adhering lecithin. The analogy between the properties of the plasma lecithin and the serum complement, as well as its relation to the middle piece of the complement, is discussed. A method for the estimation of the osmotic resistance of the corpuscles under various conditions is described. S. S. Z.

The Biochemistry of Phosphatides and Sterols. II. The Importance of Cholesterol for the Physico-chemical Properties of Cell Surface. R. Brinkman and (Frl.) E. van Dam (*Biochem. Zeitsch.*, 1920, **108**, 52—60).—It has been pointed out by Hamburger (*Pflüger's Archiv*, 1895, **141**, 230) and others that erythrocytes in salt solutions become spherical. The authors show that the slightly negative charge of the corpuscle is augmented by being in contact with the charged slide, and this increase in the charge is responsible for the change in form of the erythrocyte. In the plasma the corpuscles are surrounded by a layer of lecithin containing cholesterol in colloidal solution, which prevents the cell from being acted on by an electric charge, and therefore their shape is not altered. S. S. Z.

The Biochemistry of Phosphatides and Sterols. III. The Significance of the Functional Antagonism between Phosphatides and Cholesterol. R. Brinkman and (Frl.) E. van Dam (*Biochem. Zeitsch.*, 1920, **108**, 61—73).—Phosphatides and sterols are always present in the animal organism in definite proportions, because they function antagonistically to each other. The relative amounts of cholesterol and lecithin influence the resistance of the corpuscles, the electrical isolation of the cells, the permeability to ions of the cell surface, and the water content of the tissues. The change in quotient of these two constituents, especially througr the agency of nutrition, is of importance. A one-sided administration of lecithin to a rabbit has produced intensive hæmolysis in vivo, as well as regeneration of the blood corpuscles. S. S. Z.

Action of Electrolytes on Ricin-Hæmagglutination. Peter Rona and Paul György (*Biochem. Zeitsch.*, 1920, 105. 120—132).—The results of the authors' experiments show that the agglutination of blood corpuscles by ricin takes place solely in presence of electrolytes. The cations may be arranged in the

following series, the first having the least and the last the greatest effect on the agglutination: K, Na, Ba, also Mg, Ca. Contrary to the statements of various authors, the agglutination is influenced differently by different anions; in the series Cl, SO_4, NO_3, phosphate anion, $FeCy_6$, SCN, I, the first aids agglutination the most and the last the least. The results obtained are in agreement with Freundlich and Rona's theory, according to which the sensitisation of blood corpuscles depends on diminution of their electric charge. Roughly quantitative investigation of the cataphoretic velocities of blood corpuscles charged with ricin, and others uncharged, appeared to indicate no certain difference between these velocities.

T. H. P.

Preparation and Investigation of Thrombin. MAX BLEIBTREU and EDGAR ATZLER (*Pflüger's Archiv*, 1920, **181**, 130—140; from *Chem. Zentr.*, 1920, iii, 420).—Acetic acid is added to the serum (100 c.c.), which has been agitated with casein (1 gram), whereby the latter is precipitated, together with the adsorption compounds which it forms, with thrombin and metathrombin. The preparation is stable when dried and powdered, and does not lose its activity when preserved during a year. Active and stable thrombin solutions can be prepared from it by treatment with water and *N*-sodium hydroxide solution, neutralisation with *N*-hydrochloric acid, and purification by precipitation with colloidal ferric hydroxide, saturated magnesium sulphate solution, and alcohol (one-third to one-half volume), and these solutions have been found useful in treating hæmorrhage in animals. In an electric field, thrombin and metathrombin migrate to the anode.

H. W.

Mechanism of Pepsin Action. A. GYEMANT (*Biochem. Zeitsch.*, 1920, **105**, 155—168).—The author discusses the two principal theories of the action of pepsin, especially that according to which the function of the acid is to cause the protein to swell, and so become accessible to the enzyme. When hydrochloric acid is used, the "protein chloride" is usually a strongly dissociated electrolyte, so that, as the acidity increases to a moderately high value, the number of protein ions and the swelling must increase. This is, however, not always the case, since with serum albumin + sulphosalicylic acid, and with ricin globulin + sulphosalicylic acid, the acid causes, not swelling, but precipitation, of the protein. Digestion experiments with the heterogeneous systems thus obtained show that the optimal acidity is $p_H = 1{\cdot}7—2$; this optimum coincides with that observed with dissolved protein, although, if the swelling had any influence, displacement of the optimum would be expected. Further experiments show that the whole course of the digestion curve, as well as the position of the optimum, may be attributed solely to the concentration of the hydrogen ions by virtue of their simultaneous actions on the protein and on the pepsin. The position of the optimal hydrogen-ion concentration is never affected by the nature of the anion of

the acid, but this may in some cases, for instance, with sulphosalicylic acid, influence the absolute amount of digestion.

T. H. P.

The Significance of Gastric Hydrochloric Acid, and the Importance of the H-ion Concentration in Biological Sciences. I. Traube (*Biochem. Zeitsch.*, 1920, **107**, 295—299). —A theoretical paper.

S. S. Z.

The Problem of Nuclein Metabolism. The Formation of Uric Acid after Parenteral Administration of Purine Nucleosides in Healthy Men. Julius Rother (*Zeitsch. physiol. Chem.*, 1920, **110**, 245—253).—A rise was observed in the uric acid excretion of patients who previously received an intramuscular injection of guanosine. The author points out that, as the treated patient manifested high temperatures and other abnormal symptoms, it is possible that the increase in the uric acid may not have been due entirely to the decomposition of the guanosine, but may have been produced endogenously, owing to the disturbed condition of the patient.

S. S. Z.

Intermediate Metabolism and its Active Enzymes. Torsten Thunberg (*Skand. Arch. Physiol.*, 1920, **40**, 1—91; from *Chem. Zentr.*, 1920, iii, 390—391).—The severed muscular tissue of a recently killed frog, after being extracted with water, loses the power of decolorising methylene-blue in a medium free from oxygen; this capacity can, however, be restored by the addition of certain substances, since, under the action of an enzyme, two atoms of hydrogen are removed from the latter and transferred to the dye, with consequent formation of its leuco-base. The cells are provided with an enzyme which is specifically active towards those substances which activate the decolorising capacity, and these substances therefore probably represent intermediate stages through which the primary simple nutrient materials pass in their transformation into the final products. The author therefore considers materials such as dextrose, fats, amino-acids, etc., to undergo a series of transformations by indirect oxidation effected by "dehydrogenation." The newly discovered enzymes, in their capacity as "hydrogen transportases," bring about the removal of hydrogen from the nutrient material, which either combines with oxygen or is employed in the halogenation of other substances. According to this conception, all nutrient material, no matter of how diverse a character, must be able to yield hydrogen. The latter is the universal fuel for all cells. The replaceability of one food by another is therefore regarded in a new light.

The following substances act as powerful restorers of the lost decolorising power: formic, acetic, butyric, hexoic, succinic, fumaric, maleic, tartronic, *l*- and *dl*-malic, *l*-, *r*-, and *meso*-tartaric, *l*-α-hydroxyglutaric, citric, lactic, α- and β-hydroxybutyric, pyruvic and glutamic acids, and alanine. On the other hand, the following materials are inactive: propionic, *iso*butyric, *iso*valeric, crotonic, allylacetic, oxalic, malonic, glycollic, hydroxy*iso*butyric, methyl-

succinic, glutaric, adipic, and a number of other saturated and unsaturated dicarboxylic acids, glycine, leucine, phenylalanine, and other amino-acids, creatine, creatinine, guanidine hydrochloride, taurine, urea, and glucosamine.

It is possible to differentiate between the various enzymes from the mixture in the muscle by powerful and rapid cooling and by increase in temperature; the enzymes which act on the different acids mentioned above show a very uneven resistance to alterations in temperature and a pronounced "cryolability." H. W.

The Relation of Cholesterol to the Intermediate Stage of Fat Metabolism. W. HUECK and L. WACKER (*Biochem. Zeitsch.*, 1919, **100**, 84—99).—The free and esterified cholesterols were estimated in the total blood, the serum, and in the fresh and dried erythrocytes and leucocytes in the blood of various animals. The results are given in a table. The erythrocytes are characterised by the absence of cholesterol esters. The cholesterol in animal fat was found to be present mostly, if not entirely, as free cholesterol. Cholesterol was also fed to rabbits, and the lipoid fraction of the blood was examined in these animals as well as in normal and starving rabbits. The results show a great variation in the cholesterol content of the blood of normal rabbits. An increase was found in the total lipoids, the free and esterified cholesterol, and the lecithin in the blood of the animals which received the cholesterol. Lipæmia was observed in the starved animal. S. S. Z.

Action of the Accessory Food Factors. FRITZ VERZÁR and JOSEF BÖGEL (*Biochem. Zeitsch.*, 1920, **108**, 185—206).—The pharmacological action of extracts of the fat-soluble *A* and water-soluble *B* accessory food factors on various organs was examined. No characteristic behaviour of these factors could be established. S. S. Z.

Amino-acids in Nutrition. I. Studies on Proline: Is Proline a Growth-limiting Factor in Arachin (Globulin from the Pea-nut)? BARNETT SURE (*J. Biol. Chem.*, 1920, **43**, 443—456).—The biological value of arachin as tested on rats appears to be low, but the low content of proline is not the factor limiting growth. Evidence in support of this is given by experiments, which showed that proteins rich in proline, such as zein and gelatin, do not supplement the protein arachin. Other experiments show that the low nutritive value of arachin is not raised by additions of tryptophan, cystine, a mixture of glycine, alanine, and valine, or by the sister globulin, conarachin.

Lactalbumin supplements arachin, particularly when cystine is also added. J. C. D.

Amino-acids in Nutrition. II. The Nutritive Value of Lactalbumin: Cystine and Tyrosine as Growth-limiting Factors in that Protein. BARNETT SURE (*J. Biol. Chem.*, 1920, **43**, 457—468).—The proteins removed from milk by coagulation,

after caseinogen has been separated, do not possess a high biological value for growth in rats. Cystine and tyrosine will raise this value and supplement the protein deficiencies. Lactalbumin is not, however, a protein with an unusually low cystine content, and this suggests that the efficiency of a protein may largely depend on its constitution as well as on its composition of amino-acids. The author suggests that the opinion expressed by Osborne and Mendel (A., 1916, i, 690), that lactalbumin is a protein of high nutritive value, is founded on experiments which are open to criticism. Evidence was obtained that organically-bound sulphur and a substance giving a Millon reaction are present to an appreciable extent in protein-free milk. J. C. D.

Capillarisation in Biochemistry. RUDOLF KELLER (*Biochem. Zeitsch.*, 1920, **107**, 43—49).—A theoretical paper on capillary electricity. S. S. Z.

Taste. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1920, 41, 495—534).—Considering the facts that (1) optical isomerides have different taste, (2) substitutions always affect the taste, (3) all the compounds containing either Cohn's sapophore group or Oertly and Meyer's glucophore contain vibratory hydrogen, and (4) the taste of electrolytes is due to the sum of the tastes of molecular electrolyte, anions, cations, and complex ions, the author proposes a theory that the taste of organic substances is due to electric vibration of the sapophoric element. A detailed explanation, and examples with several hundreds of different compounds, are given. Applications of the theory in physiology, psychology, and medicine are suggested. Methods of preparation of different optical isomerides used for taste experiments are included in the last chapter. CHEMICAL ABSTRACTS.

Taste. YRJÖ RENQVIST (*Skand. Arch. Physiol.*, 1918, 38, 97—201; from *Chem. Zentr.*, 1920, i, 591).—The taste system is composed of the sensory particles and their components and the liquid or solution; it is thus a heterogeneous system, one part of which comprises the colloidal protoplasmic taste cells or nerve terminations, and the other the liquid or solution. The main changes which occur depend on alteration of surface and electrical energy. Equally marked sensations of taste must correspond with the adsorption of equal amounts of the substance by the organs of taste. The concentration necessary to induce taste with the alkali salts is an additive function of the inverse values of the rates of migration of the ions. The concentration for barium and calcium chlorides is less than that for the alkali salts, whilst for aluminium chloride a minimum value is attained. Valency is therefore an important factor, and this appears to indicate a suspensoid character of the adsorption in the system of taste. In addition to the rate of adsorption, electrical phenomena are also important in their effect on the induction of taste by different electrolytes. The phenomena of the sensation of taste produced by homologous and isomeric compounds are explicable on the

assumption that the process is one of adsorption. Experimental investigation confirms the accuracy of a deduction, from which it appears that the sensation of taste is more persistent with increasing concentration of tasted substance and increasing adsorption exponent, and with decreasing inducing concentration and rate of diffusion. The author also examines the qualities of taste, their variation with differing concentrations of electrolyte, and their relationships to the differences of potential caused by the electrolyte in the sensory system. The quality of the induced taste can be foretold with some degree of accuracy if the rate of migration of the ions of a univalent electrolyte and its concentration are known. The "compensation of taste" is a peripheral phenomenon which is observed in the sensory system; a bitter taste is not, however, compensated. The "fundamental tastes," sweet, bitter, and sour, are chosen, from which, in analogy to the Young-Helmholtz theory of colour vision, all the various sensations of taste can be compounded.

H. W.

The Inducing Value of the Sensation of Taste by certain Homologous and Isomeric Compounds. YRJÖ RENQVIST (*Skand. Arch. Physiol.*, 1920, **40**, 117—124; from *Chem. Zentr.*, 1920, iii, 425—426).—The concentrations requisite to produce the sensation of taste have been estimated for six different alkyl esters of cyanoacetic acid, the methyl and ethyl esters of oxalic, malonic, and succinic acids, the homologous monohydroxy-alcohols from methyl to octyl alcohol, and various isomeric esters of certain ether acids. In the majority of cases, the results are in agreement with the relationships established previously (preceding abstract) between the inducing concentration for taste and the coefficients of diffusion. The inducing concentrations of isomerides are approximately equal, whilst with homologous compounds they diminish with increasing molecular weight. The surface tensions of isomeric substances at the inducing concentration are determined by the drop method, and found to be approximately equal.

H. W.

Protamine from the Spermatozoa of the Japanese Mackerel, Scomber japonicus. KUNIHIKO SUMIKURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 281—310).—Crude protamine is prepared by Kossel's method, dissolved in hot water, histone is removed by precipitation with ammonia, and the filtrate is neutralised with sulphuric acid. By adding a neutralised sodium tungstate solution, a white precipitate is obtained, which is recrystallised repeatedly and dried over sulphuric acid. This product is redissolved in hot water, and $\frac{1}{2}$ vol. of 50% alcohol is added to obtain a white turbidity. Cooling over ice and the addition of ether give the oily substance, which, after being washed seven to eight times with water saturated with ether, is precipitated by alcohol (three times the original vol.). The precipitate is washed with alcohol–ether mixture and dried over sulphuric acid. Such protamine contains 20·31% N, 7·15% H, 36·48% C, 22·03% H_2SO_4, corresponding with

$C_{30}H_{71}O_9N_{14},2H_2SO_4$, which shows less nitrogen, and more hydrogen and oxygen, than scombrin, prepared from European mackerel by Kurajev. Hydrolysis gives 0·609% of ammonia-nitrogen, 0·096% of hexone base nitrogen, 71·73% of arginine nitrogen, 17·26% of monoamino-nitrogen, on the basis of 100 parts of the total nitrogen. Lysine is absent, and the presence of histidine is doubtful. The protamines of European and Japanese mackerels are probably not identical. CHEMICAL ABSTRACTS.

Proteinogenous Amines. X. The Response of the Excised Uterus to Potassium, Rubidium, and Cæsium Ions. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 579—582).—Potassium and rubidium salts in concentrations of about *N*/75 produce tonic contraction of the virgin uterus of the guinea-pig, from which the muscle does not recover until the stimulating ions are removed.

The response with cæsium is less marked. J. C. D.

Lipoids. XVII. Dilignoceryl-*N*-diglucosamine Monophosphoric Ester, a New Diaminomonophosphatide from the Brain. S. FRÄNKEL and F. KAFKA (*Biochem. Zeitsch.*, 1920, **101**, 159—171. Compare A., 1914, i, 128).—Brain dried in a vacuum at a low temperature, and freed from cholesterol by extraction with acetone, was extracted with boiling light petroleum. The concentrated petroleum fraction was extracted further with absolute alcohol. A lead compound, $C_{60}H_{111}O_{14}N_2PPb_3$, decomposition point 305—308°, was obtained from this fraction, which, unlike Thudichum's myelin, was soluble in ether. It was also soluble in benzene, but not in alcohol. By decomposing the lead salt with hydrogen sulphide, the free compound, $C_{60}H_{117}O_{14}N_2P$, m. p. 190°, was obtained. On hydrolysis, lignoceric acid, glucosamine, and phosphoric acid were obtained from this compound. It is, therefore, *dilignoceryl-N-diglucosamine monophosphoric ester.* S. S. Z.

Unsaturated Lipoids of the Liver. P. A. LEVENE and T. INGVALDSEN (*J. Biol. Chem.*, 1920, **43**, 359—378).—The unsatisfactory state of the knowledge regarding the phosphatides of the liver led the authors to reinvestigate the subject. The unsaturated lipoids of other organs have been classified as (1) acetone-soluble lipoids, consisting principally of lecithin with small proportions of cephalin; (2) acetone-insoluble, but alcohol-soluble, fraction, which consists of lecithin with larger proportions of cephalin; and (3) a fraction insoluble in acetone and alcohol, which consists of very small proportions of lecithin with larger amounts of cephalin, together with substances which are derived from the lipoids themselves.

These three fractions, with their general characteristics, were obtained from liver tissue, and in this respect the lipoid material obtained from the liver is similar to that obtained from the other organs. A study of the lecithin isolated from the liver reveals that there are two fatty acids in the molecule, one saturated, stearic

acid, and the other unsaturated and of the linolic series. No evidence of the presence of oleic acid was obtained.

The paper records progress in the attempts to prepare a pure specimen of cephalin. Preparations containing 70% have been obtained. J. C. D.

Presence of a Large Amount of Cholesterol Ester in the Liver Oil of the Basking-shark, Cetorhinus maximus, Gunner. MITSUMARU TSUJIMOTO (*Bull. Tokyo Ind. Research Lab.*, 1920, **15**, No. 2, 1—10).—So far, an animal oil has never been reported to contain more than 3% of cholesterol. The oil extracted at 100° from the liver of a young basking-shark had D^{15} 0·9176, acid number 0·301, saponification number 14·57, Wijs number 174·4, n^{20} 1·4836, butyrorefractometer at 20°, 87·2, $[\alpha]$ −2·7, unsaponifiable matter 20·55%. It contained 9% of squalene. 42% of the unsaponifiable substance is found to be cholesterol ester, corresponding with 8·6% of original oil. More than 90% of the cholesterol exists as ester, the remainder being free. By means of lipase, this cholesterol ester was separated from other fat. Whether the presence of such a large amount of cholesterol in the oil of this shark is characteristic of this fish or is due to a peculiar pathological condition which might be associated with this particular specimen has not been yet determined.

CHEMICAL ABSTRACTS.

The Monoamino-acids of the Lens of the Eye. A. JESS (*Zeitsch. physiol. Chem.*, 1920, **110**, 266—276).—The monoamino-acid content of the albumoid, the α-cristallin, and the β-cristallin of the lens of the eye has been determined. The outstanding feature of this analysis is that the alanine content of the albumoid is low, 0·8% against 2·6% and 3·6% in the β-crystallin and the α-crystallin respectively. Only traces of valine (0·2%) could be detected in the albumoid. One-half of leucine and its isomerides could be established in the β-crystallin as compared with the quantities of these substances present in the α-crystallin and the albumoid. No very striking differences in the content of the other monoamino-acids of these proteins could be established. S. S. Z.

The Capacity of the Animal Skin to React with Phenol-aldehydes. OTTO GERNGROSS (*Biochem. Zeitsch.*, 1920, **108**, 82—97).—Glycylglycine ester when treated with *o*-protocatechu-aldehyde and *o*-vanillin, respectively, yields compounds showing a golden-yellow colour similar to that obtained when skins are treated with these substances. A combination of *o*-protocatechu-aldehyde with *l*-tyrosine methyl ester yielded a similar colour. Hide powder previously treated with formaldehyde was only slightly coloured by phenolaldehydes, and this colour could be washed out. This shows that the basic groups of the skin react with the phenol-aldehydes in the ordinary way. On the other hand, treated and untreated skins gave the same coloration with sodium diazobenzene-sulphonate. The imino-group of the iminazole ring does, therefore, not react with formaldehyde. *o*-Protocatechualdehyde is capable

of tanning skins, *o*-vanillin is not. The author attributes the tanning action to the two hydroxyl groups in the benzene ring of the former compound. He also suggests the possibility that the colouring action of the phenolaldehydes is not due to the aldehyde, but to the phenol group. The colouring cannot be ascribed to the formation of a Schiff's base. S. S. Z.

Amino-acids of the Blood as the Precursors of Milk Proteins. C. A. CARY (*J. Biol. Chem.*, 1920, **43**, 477—489).—In the non-lactating cow, the level of amino-acid nitrogen is approximately the same in the blood from the mammary vein and from the jugular vein. When the mammary gland is active, however, the level of amino-acid nitrogen is very much lower in the blood in the mammary vein than in the jugular. This indicates that the proteins of the milk are built up from amino-acids brought to the gland by the arterial system.

The carbon dioxide capacity of the plasma has also been studied in both conditions, but the significance of the results is uncertain. J. C. D.

Influence of Ether or Alcohol on the Coagulation of Milk. Influence of Sodium Nucleinate on the Coagulation of Milk and Blood. M. DOYON (*Compt. rend. Soc. Biol.*, 1920, 83, 918—919; from *Chem. Zentr.*, 1920, iii, 395).—The coagulation of milk by rennet is noticeably facilitated by the presence of ether or alcohol, but retarded by sodium nucleinate; the latter effect is immediately removed by addition of calcium chloride. Blood does not coagulate, but rapidly suffers very marked hæmolysis when brought directly into sodium nucleinate; in this case, also, coagulation is immediately induced by the addition of calcium chloride. H. W.

The Technique of Urine Acidimetry (specially for Clinical Purposes). W. BIEHLER (*Zeitsch. physiol. Chem.*, 1920, **110**, 298—306).—The H-ion concentration of urine calculated from titration figures differs from values obtained by direct estimation of the H-ion concentration. By plotting curves from the values obtained by the two methods, it is seen that there is a relationship between the two sets of results. It is suggested that the real H-ion concentration can be obtained by titration and comparing the two curves. S. S. Z.

Pyrrole and Melanuria. III. PIETRO SACCARDI (*Gazzetta*, 1920, **50**, ii, 118—128. Compare A., 1919, i, 421; this vol., i, 203).—In view of the fact that by some tyrosine and by others adrenaline is regarded as the mother substance of the melanins, the author has made experiments the results of which indicate that tyrosine alone is not capable of giving rise to melanin, since it exhibits great resistance to organic and inorganic oxidising agents; adrenaline is considerably more sensitive than tyrosine to oxidising agents, and, under the action of chlorine water, yields a brown precipitate of the appearance of melanin.

Pyrrole administered by ingestion is slowly absorbed and slowly eliminated by man, and large doses are necessary to produce melanuria, since the organism partly destroys it and partly eliminates it unchanged; when injected, pyrrole is largely oxidised.

Egg-albumin, but not dextrose, yields a true melanoidal substance when subjected to protracted boiling with concentrated hydrochloric acid.

Melanins from hair, from the choroid, and from a melanotic tumour undergo vigorous oxidation when treated with peracetic acids, and yield minute, acicular or tabular crystals, which, in view of the resemblance between the phenomena of these oxidations and those of the oxidation of pyrrole-black, may consist of succinic acid or succinimide. T. H. P.

The Physiological Action of Silicic Acid. The Influence of Silicic Acid on the Animal Organism. FRANZ SCHUHBAUER (*Biochem. Zeitsch.*, 1920, **108**, 304—308).—Merck's preparation of natrium silicium purissimum is hydrolysed in the intestine by the action of water, with the formation of sodium hydroxide. This change can be obviated by neutralising the preparation.

S. S. Z.

The Physiological Action of Silicic Acid. The Absorption of Silicic Acid. FR. BREEST (*Biochem. Zeitsch.*, 1920, **108**, 309—316).—A rise in the silica content of the body can be established by increasing the silica in the food in a suitable form. Only a small portion of the administered silica is retained by the body. The author confirms Schuhbauer's results concerning the hydrolysis of Merck's silicates (see preceding abstract). S. S. Z.

Do Amino-acids Possess Secretin Characteristics? SCHWEITZER (*Biochem. Zeitsch.*, 1920, **107**, 256—267).—Amino-acids obtained by hydrolysis of protein with hydrochloric acid at 100° have shown no definite secretin action on the gastric glands. It is concluded from some of the experiments that secretin activity is not due to a single definite chemical substance, but may be produced by various compounds. S. S. Z.

The Physical Theory of Pharmacological Actions. WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1919, **101**, 54—61).—A theoretical paper in reply to Traube (this vol., i, 204).

S. S. Z.

Pharmacological Actions of the Reduction Products of Coumarin. K. FROMHERZ (*Biochem. Zeitsch.*, 1920, **105**, 141—144. Compare Ellinger, A., 1908, ii, 1060; Trendelenburg, *Arch. exp. Path. Pharm.*, 1915, **79**, 9, 190).—The author has investigated the action on various animals of hydrocoumaric acid, its lactone (melilotol), *o*-hydroxyphenylpropyl alcohol, and the ether of this alcohol (chroman). The results obtained show that, with the exception of hydrocoumaric acid, these compounds exhibit approximately the narcotic properties of coumarin, but show no

advantages, especially as regards the ratio of toxicity to activity, over the parent substance. Further, Fränkel's view ("Arzneimittelsynthese"), that coumarin is a substance which exerts narcotic effects in virtue of its carbonyl group, is contradicted, since reduction of the carbonyl to methylene does not remove the narcotic properties. Comparison of hydrocoumaric acid with melilotol appears to indicate that the lactone ring is of significance as regards narcotic action, but this indication fails when the lower stages of the reduction are reached. T. H. P.

Quantitative Studies in Chemotherapy. I. The Trypanocidal Action of Antimony Compounds. CARL VOEGTLIN and HOMER W. SMITH [with MARIAN M. CRANE, KATHERINE D. WRIGHT, and MABEL A. CONNELL] (*J. Pharm. Exp. Ther.*, 1920, **15**, 453—473).—The specific action of antimony lactate can be studied fairly accurately by following the disappearance of the trypanosomes from the blood stream of infected rats. There is a sharply defined threshold stage, below which the drug has no appreciable effect on the parasites. The process curve is an orderly one, and consistent throughout individual experiments.

J. C. D.

Quantitative Studies in Chemotherapy. II. The Trypanocidal Action of Arsenic Compounds. CARL VOEGTLIN and HOMER W. SMITH [with MARIAN M. CRANE, KATHERINE D. WRIGHT, and MABEL A. CONNELL] (*J. Pharm. Exp. Ther.*, 1920, **15**, 475—493).—Differences in the toxicity of various arsenic preparations have been explained on the hypothesis that they must be changed into one type, namely, the tervalent oxides, RAs:O, before exerting their principal toxic effect. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Metabolic Action of Bacteria. FRITZ VERZÁR and JOSEF BÖGEL (*Biochem. Zeitsch.*, 1920, **108**, 207—219).—*Streptococcus haemolyticus* forms only acid, but not alkali, with dextrose. The acidity attained by *Bacillus paratyphosus*-B and *B. proteus* is independent of the initial reaction. In the formation of acid, *B. coli communis* produces gas; on the other hand, it uses up oxygen when it forms alkali. There is no connexion between mobility and gas formation in paratyphoid organisms. Ethyl alcohol, methyl alcohol, chloroform, and formaldehyde inhibit the gas exchange of these organisms. Much smaller doses produce definite retardation. A relation between the maximum acid formation and the presence of alcohols is established. S. S. Z.

The Chemical Composition of the Tubercle Bacillus. A. GORIS (*Ann. Inst. Pasteur*, 1920, **34**, 497—546).—See this vol., i, 582.

Antagonistic Action of Calcium and Iron Salts toward other Salts as measured by Ammonification and Nitrification. J. E. GREAVES (*Soil Sci.*, 1920, **10**, 77—102).—Experiments were made on the effect produced on the bacterial activity of a fertile, sandy loam soil by the addition of calcium and iron salts. The ammonifying and nitrifying powers of the soil were first reduced by the addition of various salts, then increasing amounts of the calcium salt or the iron salt were added, and the effect on ammonification and nitrification was observed. Calcium sulphate was found to neutralise the toxic effect on ammonification of sodium carbonate, nitrate, and sulphate, calcium chloride, and magnesium chloride and sulphate. It had no antagonism to sodium chloride. Similar results were obtained in the case of nitrification, except that there was no antagonism towards sodium sulphate and calcium chloride. Thus both the anion and cation take part in the antagonism.

Ferrous sulphate was found to be antagonistic to sodium sulphate, chloride, carbonate and nitrate, and calcium chloride; ferrous chloride to sodium chloride and nitrate, calcium chloride, and magnesium sulphate; ferrous nitrate to magnesium chloride and sulphate, calcium chloride, and sodium carbonate, sulphate, chloride, and nitrate; ferrous carbonate to sodium chloride and carbonate, calcium chloride, and magnesium sulphate. The greatest effect was produced by ferrous carbonate on magnesium sulphate, in which mixture 75% of the toxic effect was neutralised. In the case of nitrification, the order differed, and the greatest effect was produced by ferrous nitrate against magnesium chloride. The quantity of iron required for maximum effect varied with the different salts, but in no case exceeded 186 parts per million.

J. H. J.

The Pharmacology of Selenium and Tellurium. I. The Action of their Acids on Bacteria. GEORG JOACHIMOGLU (*Biochem. Zeitsch.*, 1920, **107**, 300—312).—The ions of tellurous and selenious acids are much more active than those of telluric and selenic acids. The growth of moulds is scarcely affected by the action of tellurites and tellurates. Bacteria, especially of the typhus-coli group, are, on the other hand, very sensitive to the action of these substances. The author suggests the application of tellurium compounds in the chemotherapy of typhoid infection.

S. S. Z.

Oligodynamy of Silver. R. DOERR (*Biochem. Zeitsch.*, 1920, 106, 110—133).—"Oligodynamic" water, that is, water which by prolonged contact with metallic silver has become bactericidal, shows all the properties of an antiseptic. Dilution with distilled water or concentration by distillation produces the corresponding

quantitative change, but no qualitative change, in the antiseptic power; the distillate acquires no such property. If reducing substances are excluded, boiling causes no diminution in the bactericidal action of the water. The presence of sodium chloride retards this action, and that of horse serum destroys it. The antiseptic property of oligodynamic water appears to be to some extent specific, bacteria of different species exhibiting resistance in different degrees. Solutions of definite silver compounds show the same properties as oligodynamic water. T. H. P.

Oligodynamics of Silver. II. R. DOERR (*Biochem. Zeitsch.*, 1920, **107**, 207—218).—The bactericidal action of metallic silver disappears when the metal is ignited, boiled several times in distilled water, or is embedded in an agar jelly. The inactivated metal can be reactivated by being treated with very dilute solutions of a strongly dissociated acid. The oligodynamic principle of silver is dialysable, and shows the same properties of diffusion in agar jellies as silver oxide and silver nitrate. Bacteria seeded on an agar plate containing metallic silver, silver oxide, or silver nitrate grow often in two concentric rings similar to the Liesegang phenomenon. Pieces of silver embedded in a blood–agar plate produce hæmolytic zones. S. S. Z.

The Antiseptic Action of Some Chlorine Derivatives of Methane, Ethane, and Ethylene. E. SALKOWSKI (*Biochem. Zeitsch.*, 1920, **107**, 191—201).—The suitability as preservatives of methyl chloride, chloroform, methylene chloride, acetylene dichloride, trichloroethylene, and ethyl chloride was tested. Trichloroethylene, on account of its low price, of the small quantities required to be employed, and of its volatile character, was found to be the most suitable preparation. S. S. Z.

Dependence of Yeast-growth and Fermentation on Physico-chemical Phenomena. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1920, **105**, 193—198).—The author's experiments on the fermentation of dextrose solutions containing different proportions of ammonium sulphate confirm the observation that fermentation exhibits an optimum for a definite concentration of nitrogenous material. The results obtained by Pringsheim (A., 1907, ii, 287; 1908, ii, 316) with asparagine and ammonium sulphate are considered in the light of colloidal chemistry, and the conclusion is drawn that the plasma membrane of the yeast cell, somewhat in the same way as a lecithin membrane, is rendered either denser or looser by different concentrations of nitrogenous substances, the sugar thus entering the yeast cell either slowly or rapidly, and the fermentation being correspondingly slow or rapid. When peptone is used as source of nitrogen, maxima of fermentation similar to those obtained with asparagine, etc., are observed at first, the peptone being thus converted into crystalloid nitrogen compounds at the plasma membrane; this phenomenon soon disappears, owing, presumably, to the formation from the peptone of compounds which

counteract the crystalloid compounds. These membrane effects are observed also with synthetic leucine, but not with natural leucine derived from molasses. T. H. P.

Rhythmic Phenomena in the Growth and Fermentation of Yeast. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **106**, 194—206).—The processes of fermentation and of multiplication of yeast are found to exhibit a certain periodicity, which is caused by alterations in the sugar and alcohol contents of the nutrient solution. The velocity with which the yeast grows is conditioned by the concentration of the sugar, and varies irregularly as this concentration increases. T. H. P.

Course of Alcoholic Fermentation by Yeast. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **108**, 235—243).—The course of alcoholic fermentation by yeast becomes rhythmic with the increase in the concentration of the alcohol. S. S. Z.

Formation of Acid with Moulds and Yeasts. IV. FRIEDRICH BOAS, HANS LANGKAMMERER, and HANS LEBERLE (*Biochem. Zeitsch.*, 1920, **105**, 199—219. Compare A., 1919, i, 508).—The results of further experiments with yeasts indicate that different sugars act to different extents on the plasmic membrane, so that they may be arranged in order of diminishing utilisability by yeasts, as follows: maltose, dextrose, lævulose, sucrose. With many yeasts, this action on the membrane is zero with maltose and very considerable with sucrose. Such specific action of the sugars may be more or less altered, but not obliterated, by acclimatisation. Further, from the results obtained by other investigators, it appears that alteration in the reaction of the liquid and in the concentration of the nitrogenous substances may effect slight displacements in the above series of sugars. With a maltose solution containing ammonium chloride, the maximal acidity reached during fermentation was $p_H = 2{\cdot}55$, and with a whortleberry juice containing sucrose and ammonium chloride, the value $p_H = 1{\cdot}85$ was reached on brisk fermentation (compare Euler and Heintze, this vol., i, 513). T. H. P.

Maltase Solutions from Yeast. R. WILLSTÄTTER, TH. OPPENHEIMER, and W. STEIBELT (*Zeitsch. physiol. Chem.*, 1920, **110**, 232—240).—Maltase can be obtained from fresh beer yeast previously killed by an antiseptic, such as chloroform or toluene, by extracting it with water in the presence of ammonia. The authors suggest that, owing to some enzymic process, acid is formed in the yeast cell, which is responsible for the destruction of the maltase when it is extracted from the undried cell, and that the neutralising effect of the ammonia makes it therefore possible to obtain the enzyme also from the fresh yeast cell. The relation between the concentration of the enzyme and the decomposition of the maltose, as well as the velocity of the reaction, was studied

with maltase preparations from dried and fresh yeasts. The activity of maltase solutions is impaired by treatment with kaolin.
S. S. Z.

The Influence of Surface-active Nonoic Acid and of Some Surface Active Homologues of the Alcohol Series (Amyl Alcohol and Octyl Alcohol) on the Yeast Cell and on Fermentation. WILHELM WINDISCH, WILHELM HENNEBERG, and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1920, **107**, 172—190).—0·005—0·02% of nonoic acid has an inhibitive action on yeast fermentation. 0·017—0·04% of octyl alcohol has a similar effect. Higher concentrations of amyl alcohol are required to produce inhibition in fermentation. Nonoic acid and octyl alcohol also produce a diseased condition of the yeast cell, altering its appearance with the production of fat in the cell. The experiments point to the fact that the action of these substances is not due to their chemical properties, but to their surface action. S. S. Z.

Physico-chemical Considerations in connexion with Neuberg's Theory of Fermentation. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1919, **100**, 279—288); CARL NEUBERG (*ibid.*, 289—303).—A suggestion is put forward by Ostwald that physical factors, such as adsorption, might exercise some influence in the fixation of intermediate products of fermentation, such as acetaldehyde. To this Neuberg replies. S. S. Z.

The Relation of Aldehydes to Alcoholic Fermentation. CARL NEUBERG and MARTA EHRLICH (*Biochem. Zeitsch.*, 1920, **101**, 239—277. Compare A., 1918, i, 469).—The influence of seventy-one aldehydes on alcoholic fermentation was tested. It was found that the stimulating effect of the aldehyde group was general and independent of the radicle associated with it. This activation takes place whether the fermentation is produced by the living yeast or by the cell-free juice. S. S. Z.

The Relation of Phytochemically Reducible Substances to the Process of Alcoholic Fermentation and the Nature of the Action of Activators. CARL NEUBERG and MARTA EHRLICH (*Biochem. Zeitsch.*, 1920, **101**, 276—318. Compare preceding abstract).—Numerous experiments are described which show that most ketones and their derivatives and phytochemically reducible substances are capable of activating alcoholic fermentation. This activating influence is not so marked, in fact, almost absent, with the lower ketones. S. S. Z.

So-called Methyl-alcoholic Fermentation. EDMUND O. VON LIPPMANN (*Biochem. Zeitsch.*, 1920, **106**, 236—238).—Examination of twenty samples of genuine rums confirms the observation that such spirits often contain methyl alcohol in considerable proportion, as much as 7·5—8·5% of this alcohol being found in three of the samples. Much of the extraction of sugar

cane in the Lesser Antilles is carried out in presses, and the juice is subjected to inadequate clarification and mechanical purification, so that it contains considerable proportions of very fine cane fibre, which passes to a large extent into the syrups and molasses. This fibre is rich in pectinous material, and as the pectins consist of the methyl ester of pectinic acid and are readily decomposed in various ways, with liberation of methyl alcohol, the origin of the latter is evident. T. H. P.

Production of Gas during the Acetone and Butyl Alcohol Fermentation of Starch. HORACE B. SPEAKMAN (*J. Biol. Chem.*, 1920, **43**, 401—411).—From a study of the production of gas during this fermentation, a scheme is suggested to account for the substances formed which is believed to be in harmony with experimental observations, the requirements of the organism, and the conditions during fermentation.

It has been previously shown that the first two stages of the fermentation may be represented by the equations

$$(1)\ \underset{\text{Starch.}}{(C_6H_{10}O_5)_x} + xH_2O = \underset{\text{Dextrose.}}{xC_6H_{12}O_6}$$

$$(2)\ \underset{\text{Dextrose.}}{C_6H_{12}O_6} = \underset{\text{Butyric acid.}}{C_3H_7\cdot CO_2H} + \underset{\text{Acetic acid.}}{CH_3\cdot CO_2H} + [O_2]$$

The oxygen produced during the second reaction cannot be detected by ordinary chemical methods, and must therefore be used up in associated reactions, in which oxidation plays a part. Now, production of acetone commences very early in the fermentation and before the appearance of the butyl alcohol, whilst the gas given off at the commencement is pure hydrogen, but later a gradual and increasing dilution with carbon dioxide occurs. From this evidence it may be concluded that a later stage of the fermentation may be represented by the equations:

$$(3)\ \underset{\text{Butyric acid.}}{2C_3H_7\cdot CO_2H} + O_2 = \underset{\text{Acetoacetic acid.}}{2CH_3\cdot CO\cdot CH_2\cdot CO_2H} + 2H_2$$

$$(4)\ CH_3\cdot CO\cdot CH_2\cdot CO_2H = \underset{\text{Acetone.}}{CH_3\cdot CO\cdot CH_3} + CO_2$$

The intermediate formation of acetoacetic acid has not been proved experimentally, but Raistrick and Clark (this vol., i, 352) have already suggested that it occurs.

The formation of butyl alcohol, and to a much smaller degree of ethyl alcohol, takes place by the reduction of the corresponding acid:

$$(5)\ C_3H_7\cdot CO_2H + 2H_2 = CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + H_2O.$$
$$(6)\ CH_3\cdot CO_2H + 2H_2 = CH_3\cdot CH_2\cdot OH + H_2O.$$

Other points require further study, as, for example, the disappearance of a larger amount of acetic acid than can be accounted for by the amount of ethyl alcohol produced, the volume of

hydrogen and carbon dioxide given off, which cannot be accounted for by the activity of reactions previously mentioned in this scheme, and the consumption of oxygen made available by the production of butyric acid, which is not oxidised to acetone, but reduced to alcohol. J. C. D.

The Third Form of Fermentation of Sugar. CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **100**, 304—322).—In the presence of alkaline salts, sugar, when fermented by yeast, undergoes a cleavage into acetic acid, ethyl alcohol, carbon dioxide, and glycerol. This abnormal fermentation the authors call the "third form of fermentation," in contradistinction to the normal process and the process of fermentation carried out by fixing the acetaldehyde produced with an agent, such as sodium sulphite—"the second form of fermentation." Fermentation of sugar by yeast in the presence of potassium carbonate, dipotassium phosphate, magnesium oxide, trisodium phosphate, disodium phosphate, and a "buffer mixture" of monosodium and disodium phosphate, yielded products of fermentation characteristic of the "third form of fermentation." In the presence of aluminium hydroxide and colloidal iron hydroxide, the fermentation was normal. During fermentation of sugar in molar dipotassium phosphate, a sixfold production of acetaldehyde is observed in the early stages of the fermentation. This falls to the normal rate as fermentation proceeds. S. S. Z.

The Gaseous Exchanges of the Root with the Atmosphere. RAOUL CENGHELLI (*Compt. rend.*, 1920, **171**, 575—578).—In a confined atmosphere, plant roots respire in much the same way as other organs, the ratio of carbon dioxide expired to oxygen inspired varying from 0·7 to 1, according to the species. In a very moist atmosphere there is an increase in the rate of respiration, but the above ratio remains constant. When the roots are in contact with a very moist atmosphere and still attached to the aerial organs, there is further increase in the respiration, but the carbon dioxide formed is not completely expired, so that the respiratory-coefficient is low. W. G.

The Velocity of the Photochemical Degradation of Carbon Dioxide in Living Cells. OTTO WARBURG (*Biochem. Zeitsch.*, 1919, **100**, 230—270. Compare this vol., i, 583).—The velocity of assimilation of carbon dioxide is proportional to the concentration of the gas when the concentration is low. With higher concentrations, the velocity of assimilation increases proportionately less as the concentration of the carbon dioxide increases until it is no more influenced by the concentration. In the case of illuminations of low intensity, the velocity of assimilation is also proportional to the intensity of the illumination, but with higher illuminations the increase in the velocity of assimilation becomes lower as the intensity of the illumination increases.

Temperature influences the assimilation of carbon dioxide in high concentrations of the gas when intensely illuminated in a pronounced degree. Between 5° and 32°, the temperature-coefficient sinks from 4·3 to 1·6. In the case of illuminations of high intensity, more carbon dioxide is decomposed by the same quantity of energy when the illumination is intermittent than when it is continuous. This differentiation does not take place when the illumination is low. The influence of phenylurethane and of hydrocyanic acid on the carbon dioxide assimilation and on the respiration of algæ was also studied. S. S. Z.

Adsorption and Modification of Food Materials by Plants. E. Reinau (*Zeitsch. Elektrochem.*, 1920, **26**, 329—342). Corresponding with the theory of the assimilation of carbon dioxide by plants, a similar hypothesis is proposed for the other elementary food materials, and conclusions are drawn therefrom for the complete metabolism of plants; the idea of physiological concentration receives an explanation thereby. The different stages passed through by the elementary food materials are somewhat as follows: acceptor compound, assimilation substances of varying complexity, acceptor substance, acceptogen, structure material and reserve matter, degradation products. The natural periodic sequence in the formation of these different substances necessitates a continuously varying provision of the corresponding elementary food materials to the plant. To secure the highest cultural result, therefore, the metabolism for each specific element must be separately considered. The various individual metabolisms are, however, inseparably connected since the elementary food materials, singly or in conjunction, may in the form of acceptor substance chemically or physically attract another elementary food material. The hydrostatic osmotic action of carbon metabolism towards water in plants is considered, and from this point of view the connexion between the phenomena of the nutrient salt economics of plants and the height of their growth is explained. In the light of the author's theory, a simple explanation of the relationship between the increase of a vegetation factor and the mass production of plants is given. Certain peculiar phenomena observed in the carbon-dioxide manuring of plants are brought into the general scheme of metabolism.

Certain analogies to the principles of material metabolism in plants are shown when changes of energy are considered.

All the conceptions thus developed depend on the lytic properties of water and the associations and dissociations which occur within the individual cell surrounded by walls of varying permeability.

It is further shown that the elementary food materials consist of substances of low atomic or molecular weight, that the continuously increasing condensation and formation of insoluble products direct the stream of nutrient material in a definite direction, and that this action is supplemented by the behaviour of the condensation products at the differently permeable cell walls whereby the backward flow of the elementary substances is hindered. H. W.

Formaldehyde as an Intermediate Stage between the Real Assimilation and the Formation of Carbohydrates in Plants. MARTIN JACOBY (*Biochem. Zeitsch.*, 1919, **101**, 1—6).—Leaves of *Tropaeolum majus* were exposed to formaldehyde in the dark, and it was found that an increase in the dry matter took place in these leaves as compared with control leaves when certain conditions were observed. The author considers that the formaldehyde was not fixed, but actually transformed into tissue of the plant. S. S. Z.

Selective Absorption of Ions from Equilibrated Solutions. E. PANTANELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1920, 26, 136—151).—Experiments have been made on the absorption of the different ions in salt solutions by marine algæ and by terrestrial plants. T. H. P.

Distribution of Lycorine in the N.O. Amaryllidaceæ. II. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **2**, 331—334. Compare this vol., i, 467).—The crystallised alkaloid has been isolated from the bulbs and roots of *Amaryllis Belladonna*, L., *Clivia miniata*, Benth., *Cooperia Drummondii*, Herb., *Cyrtanthus pallidus*, Sims, and *Sprekelia formosissima*, Herb. (yield, 0·1—0·01% and less). It is doubtless identical with "belamarine" from the first-named species and with "amarylline" from the last-named, both isolated by Fragner (A., 1891, 1122), and also with the veratrine-like alkaloid obtained by Molle from the second species (*Jahresb. Pharm.*, 1903, 27). G. B.

Constituents of Digitalis. WILLIAM J. MCGILL (*J. Amer. Chem. Soc.*, 1920, **42**, 1893—1900).—By careful manipulation and uniform methods of procedure, using various solvents, it is possible to obtain crude fractions from digitalis which will have a reasonably constant chemical composition. The cold water extract of the leaves contains either none or a very minute quantity of digitoxin, its activity being entirely due to two fractions, soluble and insoluble in chloroform respectively (compare Kraft, A., 1912, i, 373). The digitsaponin of digitalis leaves is found to be totally inactive and non-hæmolytic when purified. The chloroform-soluble fraction obtained by Hatcher (compare *J. Amer. Pharm. Assoc.*, 1919, **8**, 913) from the hot water extract of the leaves is a mixture of gitalin and digitoxin. W. G.

The Appearance and the Emulsifying Action of Various Substances in the Cells of the Leaves of Fontinalis antipyretica. KARL BORESCH (*Biochem. Zeitsch.*, 1919, 101, 110—158).—The fatty nature of the thread-like convolutions present in the cells of the leaves of *Fontalis antipyretica* has been established by means of microchemical methods. Alcohols, phenols, alkaloids and their salts, ammonia and its salts and its derivatives, produce the disintegration of these convolutions into small drops (emulsification). The emulsifying action of substances belonging to the groups mentioned has been studied in detail. S. S. Z.

"Taifushi" Oil. S. KEIMATSU (*J. Pharm. Soc. Japan*, 1920, 283—296).—"Taifushi" oil, m. p. 22—23°, D^{15} 0·952, $[\alpha]_D$ +51·2°, acid number 12·06, saponification number 20·30, iodine number 85·05, is the oleum gynocardiæ (oleum chaulmoogræ) of the Japanese pharmacopœia, but, in the author's opinion, is obtained from neither *Gynocardia edorata*, R. Br., nor *Taraktogenos kurzii*, King, but from the seeds of *Hydnocarpus anthelmintica*, Pierre. It contains palmitin, but its chief constituents are glyceryl chaulmoograte and hydnocarpate. A dihydroxyhydnocarpic acid, $C_{15}H_{27}(OH)_2 \cdot CO_2H$, m. p. 83°, is obtained by oxidising hydnocarpic acid at a low temperature. CHEMICAL ABSTRACTS.

Phytin. XVI. Occurrence of Inositolhexaphosphoric Acid in the Seed of the Silver Maple (Acer Saccharinum). R. J. ANDERSON [with W. L. KULP] (*J. Biol. Chem.*, 1920, **43**, 469—475).—From the freshly powdered maple seed, a crystalline barium salt corresponding with tribarium inositolhexaphosphate was isolated. The freshly powdered seed does not, apparently, contain any active phytase. The examination of a sample of seed which had been stored for some time showed that some hydrolysis of the organic phosphorus compounds had occurred, for the salt isolated was apparently a barium salt of inositolpentaphosphoric acid. J. C. D.

The Biochemical Method of Detection of Glucosides Hydrolysable by Emulsin. ÉM. BOURQUELOT (*Compt. rend.*, 1920, **171**, 423—425. Compare Delauney, succeeding abstract).—A brief review of the work accomplished by this method. W. G.

Extraction of Glucosides from Two Indigenous Orchids; Identification of these Glucosides with Loroglossin. P. DELAUNEY (*Compt. rend.*, 1920, **171**, 435—437).—The author has isolated from *Orchis Simia*, Lam., and *Ophrys aranifera*, Huds., a crystalline glucoside identical in each case with the loroglossin obtained from *Loroglossum hircinum*, Ric., by Bourquelot and Bridel (A., 1919, i, 243). W. G.

The Action of Pectase. HANS VON EULER and OLOF SVANBERG (*Biochem. Zeitsch.*, 1919, **100**, 271—278).—The coagulation of the juice of *Ribes nigrum* is not due to any change in the hydrogen-ion concentration, but is brought about by the action of an enzyme. When the juice is heated at 95° or 75° for five minutes, no coagulation takes place after three days. The optimum H-ion concentration for the activity of the enzyme is $p_H = 4·3$. The pectase of *R. rubrum* coagulates the pectin of *R. nigrum*. S. S. Z.

The Formation of Melanin in Autolysed Potato Juice. HUGO HAEHN (*Biochem. Zeitsch.*, 1919, **100**, 114—129).—The dark coloration of potato juice is due to the formation of melanin by tyrosinase from the tyrosine of the juice. The "melanin value" is the number of c.c. of 0·002*N*-potassium permanganate necessary to decolorise 1 c.c. of boiled and filtered juice. During storage of potato juice at 37°, the proteins in it are autolysed and more tyrosine is set free, which is responsible for a higher "melanin

value." The difference in the "melanin value" before and after autolysis—"the autolytic value"—varies with the different varieties of potatoes. Six months' storage of the potato tuber produces an increase in the amino-acids, but a decrease in the tyrosinase. The formation of melanin is increased in weakly alkaline solution when the juice is stored in a warm place. S. S. Z.

Investigation of Plantago coronopus, L. EM. EMMANUEL and M. PAPAVASILION (*Arch. Pharm.*, 1920, **258**, 142—147).—The plant is indigenous to Greece and the surrounding countries; preparations of it are used as powerful diuretics.

The seeds yield 44·2% of mucus and 4·6% of a gum which is soluble in water, shows the reactions of the pentoses, and is converted by nitric acid into mucic acid.

The whole plant, excluding the seeds, was exhaustively extracted with alcohol (95%); the concentrated extract deposited small quantities of chlorophyll and sodium chloride. The filtrate was diluted with water containing sulphurous acid, and the precipitate formed separated by ether into insoluble *plantagenic acid*, $C_9H_{12}O_2$, m. p. 210° (the *silver* salt was analysed), and soluble resin, acid number 73·39, saponification number 158·7, from which sodium hydroxide solution extracted *coronopic acid*, $C_{54}H_{66}O_2$, amorphous, white mass, m. p. 281—282°, whilst from the portion left after this treatment a pale yellow, mobile essential oil, n^{40} 1·6893, was obtained in very small amount by distillation with steam, the remainder consisting of a *resin*, m. p. 128—130°, which evolved benzoic acid when heated on platinum foil. The presence of bitter principles or glucosides could not be detected, but emulsin and invertin were found by Bourdier's method.

The plant yields 7% of ash containing aluminium, magnesium, sodium, potassium, silica, chlorine, phosphoric and sulphuric acids; the presence of lithium could not be detected spectroscopically. The diuretic action of the plant, which has frequently been attributed to the latter element, is probably due to its high content in mucus. H. W.

The Ragweed Pollen Proteins. FREDERICK W. HEYL and HARRIS H. HOPKINS (*J. Amer. Chem. Soc.*, 1920, **42**, 1738—1743. Compare Heyl, A., 1919, i, 373).—The proteoses, the albumin, and the glutelin from ragweed pollen have been hydrolysed with 20% hydrochloric acid and the various amino-acids, etc., estimated in the product by the Van Slyke process. Histidine is entirely absent from the proteoses and albumin. W. G.

Some Constituents of Viburnum prunifolium. FREDERICK W. HEYL and CHARLES BARKENBUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1744—1755).—The dried root bark of *Viburnum prunifolium* was examined by the usual methods. Amongst the various products were acetic and valeric acids in the free state, as complex esters soluble in water and as resinous esters insoluble in water. The resin insoluble in water contained a new *phytosterol*, m. p. 186—187°, $[\alpha]_D$ +115° (in chloroform), giving an *acetate*, m. p. 223—224°. The fat from this resin contained formic, acetic, hexoic, octoic, myristic, palmitic, oleic, and linolic acids, but no

valeric acid. A trace of an amorphous alkaloid was found in the alcoholic extract. W. G.

Certain Physiological Actions of Osmium Tetroxide. RUD. SEELIGER (*Ber. Deut. bot. Ges.*, 1920, **38**, 176—184).—The wheat corn withstands for some hours, without being killed, relatively high concentrations of osmium tetroxide, although in lower concentrations this oxide retards germination, delays growth, and results in diminution of the magnitude of the organs of the young plant. The parenchymatous cells of the red beet are highly sensitive to the action of osmium tetroxide. T. H. P.

Ripening of Cereals. HEINRICH LÜERS (*Biochem. Zeitsch.* 1920, **104**, 30—81).—A new method is described of estimating acidity in organic extracts, the acid being titrated against both neutral-red and phenolphthalein in one and the same test liquid; this method gives reproducible results. An improvement is introduced into Sörensen's formol-titration method, the end-point being determined, not by means of azolitmin paper, but by titration in presence of neutral-red.

These two methods have been applied to follow the alterations in acidity, formol-titratable nitrogen, and enzymic relations of barley, wheat, oats, and rye during the last stages of ripening and subsequent storage for two months. The first two magnitudes diminish during the ripening, and, to a less extent, during storage, the acid passing into organic combination and the formol-titratable substances undergoing condensation to more highly complex compounds. In most cases the enzymic properties become more marked as ripening proceeds, but in some instances a diminution, followed by an increase, occurs; the enzymic changes taking place in the ripening and resting corn are considered from different chemical, physical, and colloid-chemical points of view. T. H. P.

Effect of various Soluble Salts and Lime on Evaporation, Capillary Rise, and Distribution of Water in some Agricultural Soils. M. I. WOLKOFF (*Soil Sci.*, 1920, **9**, 409—436). —The salts used were ammonium, potassium, and magnesium sulphates, sodium chloride, calcium nitrate, potassium phosphate, and calcium oxide, these being applied at the rate of approximately 2510 kilos. per hectare to different types of soil. The results obtained varied considerably with the particular salt used and the soil to which it was applied. In general, soluble salts materially decrease the evaporation of soil moisture, there being apparently a direct relationship between the efficiency of the salts in this respect and the osmotic concentration of the soil solution in the surface 2·5 cm. of soil. The greater this osmotic concentration, the greater is the depression of the evaporation. Of the salts studied, sodium chloride and calcium nitrate were most effective and potassium sulphate and phosphate least effective in checking the evaporation. In this respect calcium oxide was least effective in sea sand and sandy loam and most effective in clay loam.

In two of the soils sodium chloride decreased the capillary rise, whilst calcium oxide in drab clay and potassium phosphate in a silt

loam tended to increase the rise, ammonium sulphate showing no pronounced effect.

In soils treated with sodium chloride, potassium phosphate or calcium oxide there was a pronounced tendency for an increase in the water content of the top 20 cm., and soil treated with potassium phosphate or calcium oxide contained more water even in the top inch than the untreated soil, although evaporation was decreased from the treated soil. W. G.

Distribution of Titanium in Soils and Plants. GEILMANN (*J. Landw.*, 1920, **68**, 107—124).—The estimation of titanium dioxide in soils may be carried out by a modification of Hillebrand's method ("Analysis of Silicate and Carbonate Rocks," see this vol., ii, 449). Titanium dioxide is widespread in soils in proportions varying from traces to 1%, the content generally lying between 0·3% and 0·6%. Of a number of plants examined, nearly all contain titanium, which occurs in largest proportion in the green parts of the plants. Plant ashes contain from traces to 0·27% of TiO_2. T. H. P.

Acid Clay and Acid Soil. KIUHEI KOBAYASHI (*J. Chem. Ind. Japan*, 1920, **23**, 549—555).—Reviewing theories on the acidity of soil, the author attributes the acidity to the adsorptive properties of Japanese acid clay or like substances mixed with it. (Compare this vol., i, 704). K. K.

The Importance of Liming Soils containing Humus. SVEN ODÉN (*Internat. Mitt. Bodenkunde*, **9**, 375—390; from *Chem. Zentr.*, 1920, iii, 396).—The favourable influence of lime on soils containing humus depends primarily on the formation of utilisable calcium humates. In this manner, toxic acids are neutralised, and formation of acid is hindered by the calcium humate. In addition, the calcium salts displace adsorbed nutrient matter, thus rendering it available for the plant. A marked effect on irrigation is not observed, but the oxidative capacity of the humic salts is a powerful factor. H. W.

Acidity of Mineral Acid Soils. S. OSUGI and T. UETSUKI (*Ber. Ohara Inst. landw. Forsch.*, 1916, **1**, 27—52; from *Chem. Zentr.*, 1920, iii, 395—396).—When the bases of the soil are rapidly diminished by marked weathering, colloidal substances are formed which adsorb the bases; free acids are obtained when such soils are treated with solutions of salts. Since the soil contains alumina and other compounds, which are readily decomposed by hydrochloric acid, but not by acetic acid, the filtrates from soils which have been treated with the former are rich in aluminium, whilst those obtained when potassium acetate is used contain but little of this metal. The differing intensities of the acidities of the filtrates thus obtained depend, in the first place, on the acid which has been liberated by the adsorption process in the soil. An acid soil must therefore be regarded as one which is incompletely saturated with bases. H. W.

General and Physical Chemistry.

Refractivities of Saturated and Unsaturated Compounds. GERVAIS LE BAS (*Trans. Faraday Soc.*, 1920, **15**, 231—237).—Further applications of the author's calculations to organic compounds (see A., 1918, ii, 49, 281). Negative anomalies are found with furfuraldehyde and thiophen. In pyridine there is an anomaly equal to that due to two and a-half ethenoid linkings. Other aromatic compounds, and substances containing the carbonyl group, are considered. J. R. P.

Size of the Alkali Cations and Halogen Anions. ADOLPH HEYDWEILLER (*Zeitsch. Physik*, 1920, **1**, 393—394).—Refraction data are used as a check on values obtained by Born and Landé from Born's crystal-grating theory. For the methods, previous papers are referred to. The agreement is considered excellent, and favourable to Born's theory. CHEMICAL ABSTRACTS.

A Simple Spectrometer for Laboratory Use. GÜNTER SCHEIBE (*Zeitsch. physiol. Chem.*, 1920, **110**, 229—232).—A description of a comparatively inexpensive form of spectrometer which has sufficient accuracy for ordinary purposes in a physiological laboratory. S. S. Z.

Spark Spectra of Various Elements in Helium in the Extreme Ultraviolet. J. C. MCLENNAN and A. C. LEWIS (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 109—114).—The new wave-lengths 1745 Å.U., 1742·5 Å.U., and 1657 Å.U., have been observed in the spectrum of silicon. The spectra of tellurium, molybdenum, and zirconium were examined, and the results tabulated. These are considered to be correct to 0·5 Å.U. A strong doublet appears common to all the spectra in the neighbourhood of 1745 Å.U., probably due, according to Lyman, to silicon. A strong line at 1656·7 Å.U. was found on all the plates, which Lyman gives as present in all metallic spark spectra in helium. It was probably due to carbon from the decomposition of carbon monoxide given off from the wax joint. In the spectra of molybdenum and zirconium all the wave-lengths observed were of weak intensity. The radiations from tellurium were stronger, and their relative intensities are given in the table. A reproduction of the spectrum of this element is given. J. R. P.

Arc Spectra in Vacuum and Spark Spectra in Helium of Various Elements. J. C. MCLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 95—108. Compare A., ii, 458, 459).—The vacuum arc spectra of antimony, bismuth, calcium, magnesium, selenium, silver, and copper, and the spark

spectra in helium of antimony, bismuth, cadmium, lead, magnesium, thallium, and tin, have been investigated in the region below 1850 Å.U. The work with the vacuum grating spectrograph has resulted in the extension of the vacuum arc spectrum of copper to about 1216 Å.U. J. R. P.

Air Lines in Spark Spectra from λ 5927 to λ 8719. PAUL W. MERRILL (*Astrophys. J.*, 1920, **51**, 236—243).—In observing the spectrum of any element, if the source is the spark in air, there are a large number of lines due to the air itself, which it is impossible to eliminate. In order to be able to distinguish the lines due to the various components of the atmosphere, the author has observed the spark in air and in oxygen, using several different elements as electrodes. The wave-lengths of 58 air lines are given in a table. Because of the ill-defined nature of these lines, the accuracy is not very great. Twenty of the list correspond with known lines of hydrogen, nitrogen, oxygen, or argon, including six lines of the red spectrum of argon and four of oxygen lines which had not previously been observed in spark spectra. Two others are probably due to oxygen; the rest have not as yet been identified. All the identified lines are found to be shifted toward the red with respect to vacuum tube wave-lengths. This increase in wave-length amounts to about 0·1 Å. for the oxygen lines, 0·6 Å. for the argon lines, 0·7 Å. for the hydrogen α-line, and varies from 0·1 Å. to 0·7 Å. for the nitrogen lines. On introducing self-induction the only marked change is the weakening of the nitrogen lines λλ 6482 and 6610. Using as source the condensed spark in an atmosphere of commercial oxygen, several identifications of oxygen and nitrogen lines previously observed in the vacuum tube were confirmed, and the doubtful identification of λ 7157 as due to oxygen is strengthened. CHEMICAL ABSTRACTS.

Vacuum Grating Spectroscopy. J. C. McLENNAN (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 114—123).—It would appear that in the spectroscopy of the ultraviolet the procedure to be followed which would permit of the most rapid progress being made would be, so far as emission spectra are concerned, to work with a vacuum grating spectrograph and to use an atmosphere of helium. There is evidence to show that this gas is transparent to wave-lengths as short as 400 to 500 Å.U., or even shorter. As regards absorption spectra, it is shown that if a vacuum grating spectrograph, provided with a lamp of the "Pointolite" type, is filled with helium to a suitable pressure, arcs can be struck in the gas, when the requisite voltages are applied, which will provide a radiation consisting of wave-lengths extending probably near to 400 Å.U. By interposing vapours of elements between the arc and the grating of the spectrograph, it should be possible to obtain the absorption spectra of the elements vaporised. An improved apparatus is described, and preliminary measurements made down to 1025·8 Å.U., although indications were obtained on all the plates of a

faint continuous spectrum extending to well below 500 Å.U. The potential fall between the electrodes was only 45 volts. J. R. P.

Existence of a Relation between the Heads of Banded Spectra. TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919. [3], **1**, 332—343. Compare this vol., ii, 140).—The relations $\lambda/\lambda' = \sqrt{m/m'}(p/q)^{3/2}$ and $p/q = a/a'$ between the heads of bands due to different elements of the same group in the periodic system, where λ and λ' are the wave-lengths of the heads of the bands, m and m' the atomic weights, p and q integers smaller than ten, and a and a' the radii of the atomic models of Nagaoka, are open to the criticism that there are so many heads in the spectra of the gold group and the alkaline earth group examined previously that the above relations may have been due to chance. In the present paper, by choosing elements the spectra of which have few heads, such as palladium and nickel, it is shown that the above relations hold only for elements in the same group, and do not hold for elements of different groups. Other elements for which the relations hold are vanadium, columbium, and tantalum. The conclusion is drawn that the oxide of vanadium at the moment of emission of band spectra assumes the form VO_2 and not V_2O_5, which is the form stable at ordinary temperatures.

CHEMICAL ABSTRACTS.

Fluorescence of the Uranyl Salts. EDWARD L. NICHOLS, HORACE L. HOWES, ERNEST MERRITT, D. T. WILBER, and FRANCES G. WICK (*Carnegie Inst. Washington Publication*, 1919, **298**, 1—241).—The historical introduction is followed by chapters devoted to: structure of fluorescence spectra; preliminary observations on certain uranyl salts; phosphorescence of the uranyl salts; intimate structure on cooling to −185°; polarised spectra of double chlorides; the nitrates and phosphates, water of crystallisation, crystalline form; the acetates; the sulphates; and frozen solutions. Since the fluorescence of certain uranyl compounds is resolved into groups of narrow line-like bands when these compounds are excited to luminescence at very low temperatures, a study of the fluorescence has been undertaken. The spectra of numerous uranyl salts have been mapped. Owing to the extraordinarily complex character of the phenomena, no satisfactory theory has as yet been evolved, but the mass of facts recorded and the general principles established will, it is hoped, afford a basis for the successful theoretical development of this important and little understood branch of the science of radiation. Appendices are devoted to the chemistry and crystallography of the uranyl salts, and to the subject of phosphoroscopes. CHEMICAL ABSTRACTS.

Optical Rotation, Optical Isomerism, and the Ring Electron. H. STANLEY ALLEN (*Phil. Mag.*, 1920, [vi], **40**, 426—439).—A theoretical paper in which an hypothesis of optical rotation is advanced in which the electron, instead of being

regarded as a point charge, is looked on as an anchor ring of negative electricity rotating rapidly about its axis as suggested by Parson (Smithsonian Misc. Coll., No. 2371, Nov., 1915). Such a ring electron vibrating in a linear path takes the place of an ordinary electron moving in a spiral path as postulated by Drude. It is shown that a rotation of the plane of polarisation of light will result, and an expression is found for the amount of rotation per unit length. Employing the theory of atomic structure due to Lewis and Langmuir (A., 1916, ii, 310; 1919, ii, 328), a graphical representation may be obtained for the dextro- and lævo-rotatory forms of a compound. The experimental facts with regard to optical activity are in good agreement with the hypothesis put forward, which may be applied not merely to carbon compounds, but to any compound containing an asymmetric atom. On the assumptions made it is possible to deduce that eight isomerides of cinnamic acid may exist. J. F. S.

Influence of Constitution on the Rotation of Optically-active Substances. XI. Normal and Abnormal Rotation Dispersion and its Calculation. H. RUPE and ARTHUR AKERMANN (*Annalen*, 1920, **420**, 1—32. Compare A., 1917, i, 539, and previous abstracts).—An examination of more than fifty dispersion curves leads the authors to the conclusion that the normal rotatory dispersion of organic substances can be expressed by the simple formula $\alpha_n = K_0/\lambda_n^2 - \lambda_0^2$, in which K is the "rotation constant" and λ_0^2 is the dispersion constant; the expression has been used previously by Lowry and Dickson (T., 1915, **107**, 1173). The formula is shown to be applicable to liquids in substance and in solution; it gives results which are in good harmony with the observed data over the visible spectrum, and can probably be also employed outside these limits.

In previous communications, Rupe has endeavoured to distinguish between normal and abnormal rotatory dispersion on the basis of the displacement of the "characteristic wave-length"; it now appears that when a substance exhibits abnormal dispersion within the region of measurement, the characteristic wave-length differs from the mean of the respective class of compounds, but although strong displacement is necessary for abnormal dispersion, it is not by itself sufficient.

The methods of calculating the values of K_0 and λ_0^2 are fully discussed, and it is shown that, provided the dispersion is normal, the calculated values for the specific rotations of a large number of compounds for a given wave-length agree with the values observed within the limits of experimental error. The following criteria of abnormal dispersion are then deduced, in which three types are distinguished: (i) Apparently normal rotatory dispersion with greatly displaced dispersion curve; the divergence between the calculated and observed values does not amount to more than three times the mean experimental error, but λ_0^2 and λ_n differ markedly from the mean value for the appropriate class of compound.

(ii) Relative abnormal rotatory dispersion, in which the differences are from three to five times as great as the mean experimental error; and (iii) Total abnormal rotatory dispersion, in which the differences exceed fifteen times the mean experimental error.

The connexion between optical activity and constitution is discussed at length, and it is pointed out that comparisons between molecular rotations observed with a single wave-length are inadequate for the elucidation of the problem, and that the rotatory dispersion must also be ascertained. The latter is greatly influenced by the solvent used, and, at present, this action does not appear to be exerted in any regular manner even towards substances of the same type. The influence of constitution on K_m is described, and it is found that if the added radicle is an aliphatic saturated hydrocarbon group and if the chemical change does not involve any considerable change in the optical properties of the asymmetric complex, K_m remains approximately constant in homologous series. The rule also applies when aromatic groups are introduced, provided that at least one methylene group lies between the aromatic radicle and the asymmetric complex. K_m is increased by the introduction of one or more ethylenic linkings, by a triple bond (the effect of this is noticeably less than that of two double bonds), and by the direct attachment of an aromatic nucleus to the asymmetric complex. Changes in K_m are also induced by one or more groups containing oxygen. It thus appears that K_m is not affected by the number of groups required to form the molecule, but is mainly dependent on the spatial distribution of the atoms and the relative distances from one another. H. W.

Activation of Photochemical Elements with Silver Haloid Electrodes and their Application. SATOYASU IIMORI and TOSHIMASA TAKEBE (*J. Tokyo Chem. Soc.*, 1920, **41**, 77—185). —The mechanism and sensitisation of the Becquerel effect and the application of the photochemical cell for measuring candle-power are extensively considered. In order to obtain the most stable maximal photovoltaic effect the silver haloid electrodes are prepared as follows: A small silver plate is soaked in haloids of iron, copper, mercury, or thallium; later its surface is freed from the solutions by use of suitable solvents, and it is placed in a solution of iodine in alcohol, benzene, chloroform, or ether. The final coating of the electrodes with iodide is perfected by placing them in 0·3—5 *M*-potassium iodide saturated with silver iodide. Such an electrode, after several days, becomes exceedingly sensitive, and contains a permanent film. Proper concentration of potassium iodide is very important. The cells of 20 c.c. and 90 c.c. capacity are made of glass, with ebonite covers. The outer surface is covered with tin foil except the window, which admits the light and behind which one of the electrodes is placed. A solution of potassium iodide is also used for the cell. The *E.M.F.* is measured by Poggendorff's method, the Weston cell being used as standard. Several factors for obtaining maximal photovoltaic effect are studied. The effect of

concentration of the cell liquid is expressed by $\pi_m = A + B \log 1/C$, in which π_m is in millivolts, C = concentration of potassium iodide, A and B are constants due to temperature, degrees of illumination, electrodes, etc. Rise of temperature lowers the effect, its extent depending on the illumination and characters of the cell. The effect of intensity of illumination is expressed by $\pi_m = \sigma(1 - e^{-KE\alpha})$, where E is the intensity; σ, K, and α are constants for cells, temperature, and wave-length. For a limited condition, a much simpler formula, $\pi_m = a \log E - b$, can be used. The effect of the size of windows is given by $\pi_m = \rho(1 - e^{-hA\beta})$, where A = area of window, which is always smaller than that of the electrode, and ρ, h, and β are constants. The time required to attain the maximal effect is greater with rise of temperature and concentration of potassium iodide, and smaller with increase of illumination and size of the window. The time required to decrease to the half of the maximal value after the light is removed is greater with the larger concentration of the liquid, but is independent of the intensity of illumination and the size of the window. Theoretical explanations for all factors are given. Considering the effect of temperature and nature and concentrations of the liquid used for the battery, it is concluded that the photovoltaic effect produced with haloid electrodes must be caused by reversible chemical reaction of the silver iodide, which takes place in the following order: at the exposed electrode $mn\,\mathrm{AgI} \longrightarrow mn\,\mathrm{Ag} + mn\,\mathrm{I}$, $mn\,\mathrm{I} \longrightarrow m\,\mathrm{I}'n + m\oplus$ becoming $\ominus$; at the unexposed electrode, $mn\,\mathrm{AgI} \longrightarrow mn\,\mathrm{Ag} + m\,\mathrm{I}'n + m\ominus$, $mn\,\mathrm{AgI} + m\,\mathrm{I}'n \longrightarrow mn\,\mathrm{AgI} + m\ominus$, $mn\,\mathrm{AgI} \longrightarrow mn\,\mathrm{AgI} + m\oplus\ominus$. $\oplus\ominus = 96540$ coulombs. CHEMICAL ABSTRACTS.

The Mechanism of Chemical Actions Provoked by X-rays. A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 627—629).—The mechanism suggested is that the cause of the chemical action is the destruction of the negative ions, which alone can lose their electrons by the impact of the rapid electrons constituting the corpuscular radiation. The corpuscles, slowly expelled, neutralise the adjacent positive ions, the electronegative and electropositive elements thus being liberated in the atomic state. These produce colorations in solid or viscous substances and chemical changes in media where they are mobile. Several reactions are examined in the light of this hypothesis. W. G.

Explanation of Röntgen Spectra and the Constitution of Atoms. ADOLF SMEKAL (*Physikal. Zeitsch.*, 1920, 21, 505—506).—The theories of Vegard (A., 1919, ii, 129) and of Kroo (A., 1918, ii, 303) are discussed. The calculations of Vegard do not do justice to the most exact measurements of Siegbahn (A., 1919, ii, 261), whereas the formula of Kroo appears to apply with great accuracy. The conclusions of Vegard as to the structure of atoms are thereby vitiated. J. R. P.

The X-ray Absorption Spectra of Phosphorus. J. BERGENGREN (*Compt. rend.*, 1920, **171**, 624—626).—In the

X-ray absorption spectra of the different varieties of phosphorus, the author finds that the wave-lengths of the limits of absorption are different for black phosphorus and for phosphorus in the form of phosphoric acid. That of red phosphorus shows a double limit, one component of which is identical with that of black phosphorus, and the other, attributed to yellow phosphorus, coincides, at least approximately, with that of phosphoric acid. W. G.

The Fine Structure of the Discontinuities of Absorption in X-ray Spectra. M. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 626—627).—A discussion of Kossel's work (compare *Zeitsch. Physik*, 1920, 1, 119) in the light of Bergengren's work on phosphorus (compare preceding abstract).

W. G.

Precision Measurements in the K-series of X-rays. Elements from Copper to Sodium. ELIS HJALMAR (*Zeitsch. Physik*, 1920, **1**, 439—458).—Siegbahn's vacuum spectrograph has been used in making wave-length measurements. Several new weak lines are found, besides the component of β predicted by Sommerfeld. These are: one in the neighbourhood of β, a close doublet of shorter wave-length than $\alpha_3\alpha_4$, and a line between α_1 and α_3. Not all these occur in any one element. The relation $n_\lambda = 2d \sin\phi$ is tested by comparing the angle of reflection of the same line in different orders. The lattice constant for gypsum is measured as $\log 2d = 1{\cdot}1805620{-}8(\pm 0{\cdot}0000149)$.

CHEMICAL ABSTRACTS.

Origin of the Iodine Band Spectrum and its Place in the Quantum Theory. W. STEUBING (*Zeitsch. Physik*, 1920, **1**, 426—430). The iodine band spectrum results from neutralisation of the ionised atoms and their combination to form the molecule. The high frequency limit of the spectrum gives, on the quantum theory, the work necessary for the decomposition from molecules to ions. This has been calculated by Born (A., 1919, ii, 214) on the space-lattice theory, and the agreement is quantitative. CHEMICAL ABSTRACTS.

Fine Structure of the Near Infra-red Absorption Bands of the Halogen Acids. WALTER F. COLBY (*Astrophys. J.*, 1920, **51**, 230—235).—A quantum theory of the fine structure in the infra-red absorption spectra of the diatomic gases is put forward. The postulate of Bjerrum (*Nernst Festschrift*, 1912, 90), that the fine structure of these bands is due to the rotation of the molecules in stationary states corresponding with the quantum relation, has proved very fruitful. The present paper proposes to test the hypothesis by comparing the theoretical results for the simplest molecule model of the Bohr type with the experimental results recently obtained by Imes (*Astrophys. J.*, 1919, **50**, 251) for the halogen acids. For hydrogen fluoride, chloride, and bromide, the observed interatomic vibration frequencies are

respectively 38, 40, and 47% less than the theoretical, whilst the computed separations of the pairs of nuclei are, respectively, 38, 54, and 59% less than the values given by Imes. The variation with mass is explained as a screening effect which has been neglected in the elementary theory. The agreement between theory and experiment is sufficient to lend support to the Bjerrum hypothesis, and suggests the importance of developing a more adequate theory involving fewer simplifying assumptions.

CHEMICAL ABSTRACTS.

Structure of the Helium Atom. IRVING LANGMUIR (*Science*, 1920, **51**, 605—607).—The ionisation potential as calculated from Bohr's theory, 28·8 volts, does not agree with the experimental value, 25·4 volts. By means of Landé's theory of the transference of momentum from one electron to another around the nucleus rather than a rotation of the electrons themselves, the author has calculated the numerical dimensions of the path of the electrons in the helium atom after four approximations to within 0·1%. Each electron travels through less than half an orbit when it is reflected back on approaching the other electron.

CHEMICAL ABSTRACTS.

Helium and Parhelium. J. FRANCK and F. REICHE (*Zeitsch. Physik*, 1920, **1**, 154—160).—There are two separate systems of spectral series for helium which belong to helium and to parhelium. In helium the electron orbits are coplanar, whilst in parhelium they are at an angle to each other, as described by Landé. Parhelium is the less stable, and its ionisation potential is the one determined experimentally. The base line for the principal series for helium is 10,830 Å. and for parhelium is 20,582 Å., and is caused by the return, in each case, to a diquantal orbit. For normal helium, that is, uniquantal, the resonance potential, in agreement with the calculations of Landé, would lead to a ground line of about 600 Å. A change from a higher quantum orbit of one system to a lower of the other never occurs. Parhelium is the normal condition of the element (uniquantal).

CHEMICAL ABSTRACTS.

Aggregate Recoil during the Decomposition of α-Radiating Substances. ROBERT W. LAWSON (*Wien Anz.*, 1919, 86—88; from *Chem. Zentr.*, 1920, iii, 431).—It has been observed repeatedly that polonium which has been deposited electrolytically on metallic foil activates objects in its immediate vicinity. The following explanation of the phenomenon is advanced. The polonium lies on the metallic support in aggregates of atoms. When an α-particle is discharged from such an aggregate, the latter receives the recoil in the opposite direction and leaves the support. The author designates the phenomenon "aggregate recoil," and examines its dependence on the nature of the supporting metal and on the prevalent gas pressure. The importance of the recoil on the estimation of the life period of polonium is discussed.

H. W.

Rapid Graphic Method of Estimating Radium. N. E. DORSEY (*Physical Rev.*, 1919, **14**, 173; from *Chem. Zentr.*, 1920, iii, 399).—The increase in the γ-radiation of a radium preparation from the time t_1 to t_2 is denoted by the expression $J_2 - J_1 = 1{\cdot}0089 . e^{-\lambda t_1}(1 - e^{-\lambda(t_2 - t_1)}) . J_\infty$, where λ is the rate of decay of the emanation and J_∞ the equilibrium value. If the observed values of J are plotted against $(1 - e^{\lambda t})$, in which t is calculated from any desired instant, a straight line is obtained, the intersection of which with the ordinate for $t = \infty$ gives the equilibrium value J_∞, which can thus be graphically determined. H. W.

Radium Content of the Rocks of the Loetschberg Tunnel. J. H. J. POOLE (*Phil. Mag.*, 1920, [vi], **40**, 466—471).—The radium constant of 82 specimens of rocks collected at different points in the Loetschberg Tunnel has been estimated by the fusion method. The content is found to be fairly constant throughout the whole length, a mean value $2{\cdot}2 \times 10^{-12}$ grams per gram of rock being obtained. This value is obtained from values lying between $0{\cdot}8 \times 10^{-12}$ from a talc schist obtained 480 m. from the south end of the tunnel, and $6{\cdot}5 \times 10^{-12}$ from a felspar talc schist obtained 395 m. from the south end. For individual rocks, the following mean values were obtained: granite (7 specimens), $2{\cdot}3 \times 10^{-12}$; limestone (16 specimens), $1{\cdot}5 \times 10^{-12}$; talc schist (16 specimens), $2{\cdot}0 \times 10^{-12}$; quartz schist (12 specimens), $2{\cdot}4 \times 10^{-12}$; mica schist (2 specimens), $2{\cdot}1 \times 10^{-12}$; hornblende schist (2 specimens), $3{\cdot}1 \times 10^{-12}$; schist lustré (2 specimens), $3{\cdot}4 \times 10^{-12}$; felspathic schist (3 specimens), $2{\cdot}7 \times 10^{-12}$; unclassified schists (16 specimens), $2{\cdot}5 \times 10^{-12}$; aplite (2 specimens), $2{\cdot}5 \times 10^{-12}$; quartz porphyry (1 specimen), $2{\cdot}5 \times 10^{-12}$; anhydrite (2 specimens), $1{\cdot}1 \times 10^{-12}$; and quartz sandstone (1 specimen), $4{\cdot}3 \times 10^{-12}$. The mean radium constant of 53 schists is $2{\cdot}4 \times 10^{-12}$ grams per gram of rock. J. F. S.

Atmospheric Electricity. LXI. Measurement of the Radium Emanation Content of the Air at Innsbruck. RELY ZLATAROVIC (*Wien Anz.*, 1920, 75; from *Chem. Zentr.*, 1920, iii, 334).—By the use of charcoal and petroleum as absorbents, an ionisation vessel which previously showed a saturation current, i_1, was completely freed from emanation; the saturation current, i_2, which was now measured, was found to be constant. The difference, $i_1 - i_2$, is applied to the calculation of the emanation content, and, as a mean of forty-nine observations, gives the value 433×10^{-18} Curie/c.c., the extreme values being 1110 and 40. Dependence on meteorological factors could only be so far recognised in that rainy periods correspond with lower emanation values. H. W.

Effects of Electron Collisions with Atmospheric Neon. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [A], **98**, 124—146).—The minimum radiation velocity was found to be 11·8 volts with neon at an average pressure of 0·133 mm. *

The minimum ionisation velocity was found to be 16·7 volts. The second radiation velocity was found to be 17·8 volts. The second and third ionisation velocities were found to be 20·0 and 22·8 volts respectively. The existence of three critical ionisation velocities and two critical radiation velocities indicates that neon differs more in constitution from helium and argon than would be expected from its position in the table of the elements. The accepted view of the connexion between the quantities of energy required for the production of radiation and of ionisation is that they correspond with the first and with the limiting frequency, respectively, of some particular spectral series of the element concerned. On this view, it would be expected that with every ionisation velocity there would be associated a definite radiation velocity. In the experiments, evidence of three ionisation velocities, but of only two radiation velocities, was obtained. The two radiation velocities may occur so close together that they do not give separate indications on the curves, in which case one might escape detection. Another possibility is that the ionisation observed at one of the three critical velocities is a spurious effect. The minimum radiation velocity of helium is 20·4 volts, close to the value 20·0 volts found above. The radiation velocity of 11·8 volts appears to be associated with the ionisation velocity of 16·7 volts, and the radiation velocity of 17·8 volts with the ionisation velocity of 22·8 volts. If neon consists of two or more constituents having different radiation and ionisation velocities, the critical velocities 11·8 and 16·7 are to be attributed to one, and the values 17·8 and 22·8 to the other. J. R. P.

Constancy of the Ratio of Actinium to Uranium in Natural Minerals. STEFAN MEYER and VIKTOR F. HESS (*Sitzungsber. K. Akad. Wiss. Wien*, 1919, **128**, [2*a*], 909—924; from *Chem. Zentr.*, 1920, iii, 435—436).—It has been assumed for a long time that the actinium series is derived by indirect degradation of the uranium–radium series. If this is the case, the ratio of actinium to uranium or radium must be constant in all uranium minerals. Few, and not very concordant, observations have been recorded, chiefly by Boltwood, in this connexion. The authors have therefore examined exhaustively the reputed constancy of the ratio Ac:U, and have used uranium minerals which differ as widely as possible from one another, both in origin and composition, and include the following: amorphous Joachimsthal pitchblende, crystalline pitchblende from Morogoro, bröggerite, and two different specimens of thorianite. Quantities of the minerals corresponding with 30 grams of uranium were dissolved in concentrated nitric acid, and the solutions were diluted with water to 1 litre and brought into rotating flasks; the radium emanation was first removed in a constant current of air, and, immediately afterwards, the active precipitate of actinium (with a portion of thorium precipitate if present) was collected on a negatively charged plate. The value of Ac-$B+C$ could be readily derived from the known half life-periods for Ac-$B+C$ and

Th-$B+C$. The observed activities are not great, but the results of repeated measurements are quite concordant. The ratio Ac:U is found to be constant in all minerals, thus giving a sure support for the hypothesis that the actinium series is genetically related to uranium. H. W.

Ionisation in the Solar Chromosphere. MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 472—488).—From a discussion of the high-level chromospheric spectrum, it is shown that this region is mainly composed of ions of calcium, barium, strontium, scandium, titanium, and iron, whilst in the lower layers both ions and atoms occur. An attempt is made to account for these facts from the point of view of Nernst's theorem of the reaction isobar, by assuming that the ionisation is a type of reversible chemical process taking place according to the equation $Ca \rightleftharpoons Ca^{+} + e - U$. The energy of ionisation, U, can be calculated from the ionisation potential of the elements. For the determination of the chemical constant and the specific heat, the electron is assumed to be a monatomic gas with an atomic weight 1/1836. The equation shows the great influence of pressure on the relative degree of ionisation. The almost complete ionisation of calcium, barium, and strontium in the high-level chromosphere is due to the low pressure in these regions. The calculated values are in good agreement with the experimental values of King (*Astrophys. J.*, **48**, 13). Hydrogen is completely dissociated into atoms at all points in the solar atmosphere. It is also shown that the greater the ionisation potential of an element, the less readily does ionisation occur under a thermal stimulus. Calculations have been made in the case of hydrogen ($V=13{\cdot}6$ volts) and helium ($20{\cdot}5$ volts) which show that these elements are not ionised to an appreciable extent anywhere in the sun. Helium is ionised only in stars of the highest temperature ($>16000°$ K), which therefore alone can show the Rydberg line 4686 and the Pickering lines $\nu = N[1/2^2 - 1/(1+1/2)^2]$. J. F. S.

Relative Ionisation Potentials of Gases as Observed in Thermionic Valves. G. STEAD and B. S. GOSSLING (*Phil. Mag.*, 1920, [vi], **40**, 413—425).—A method is described whereby the ionisation potential of gases may be determined. This method consists in determining the differences of potential which are necessary for the production of positive ions in soft thermionic valves. The tube used was a three-electrode valve of the usual form, the cold electrodes being connected together. Next to the tungsten filament there was a molybdenum spiral, 0·4 mm. diam., coiled into a helix of 4·5 mm. diam., and having four to five turns per cm. Outside this was a nickel cylinder 10 mm. diam. When an appreciable quantity of a gas is present in such a tube, the voltage-current curve changes, at a definite potential, from the high vacuum characteristic. This point represents the beginning of the emission of positive ions and gives the ionisation potential of the gas. Experiments have been carried out with mercury

vapour, argon, hydrogen, carbon monoxide, nitrogen, and helium at several pressures, and the following values found for the ionisation potential: mercury, 10·8 volts; argon, 12·5 volts; hydrogen, 15·0 volts; carbon monoxide, 15·0 volts; nitrogen, 17·2 volts; and helium, 20·8 volts. The value obtained for carbon monoxide differs from that obtained by other observers, and it is suggested that this does not represent a true ionisation potential, but rather a photoelectric effect. The present method of work is not open to the criticism offered to most methods of determining ionisation potentials. J. F. S.

Effect of a Trace of Impurity on the Measurement of the Ionisation Velocity for Electrons in Helium. FRANK HORTON and DORIS BAILEY (*Phil. Mag.*, 1920, [vi], **40**, 440—450). —The ionisation potential of helium has been redetermined with perfectly pure gas and the effect of impurities on this value investigated. The results emphasise the importance of maintaining the helium perfectly pure when investigating the ionisation of gas by electron collisions. The only satisfactory method when a glass apparatus is used is to have a slow circulation of freshly purified helium through the ionisation chamber during the experiments. It is possible that if fused silica were substituted for glass, contamination of the gas would be less likely to occur. The ionisation curves indicate that the minimum ionisation velocity for electrons in helium is 25·0 volts, a value rather lower than that obtained by Horton and Davis (A., 1919, ii, 210). The present results also indicate that the minimum radiation velocity for electrons in helium is 21 volts; but this value is no doubt too high, for the point at which ionisation of the impurities by the helium radiation was detected depended on the amount of impurity present, and was probably always higher than the point at which radiation was first produced from the helium atoms. J. F. S.

Ionisation Potential of Hydrochloric Acid and the Electron Affinity of Chlorine. PAUL D. FOOTE and F. L. MOHLER (*J. Amer. Chem. Soc.*, 1920, **42**, 1832—1839).—The experiments indicate that the collision of an electron of sufficient velocity with a molecule of hydrogen chloride results in the immediate production of a positively charged atom of hydrogen and a negatively charged atom of chlorine. The ionisation causes disruption of the bond between the two ions in the molecule. The work necessary to ionise a gram-molecule of hydrogen chloride is accordingly the work of ionising a gram-atom of hydrogen plus the heat of formation of hydrogen chloride plus the heat of dissociation of 0·5 gram-molecule of chlorine minus the electron affinity of a gram-atom of chlorine. This, expressed in volts and referred to a single molecule, is 13·7 volts, in excellent agreement with the experimentally determined value, 14·0 volts. The electron affinity of chlorine is calculated as 4·8 volts. Hydrogen chloride is not known to possess any characteristic visible or ultraviolet

spectrum, in agreement with the observed peculiar type of ionisation and the absence of a resonance potential. Any radiation emitted which is characteristic of hydrogen chloride would be produced by the union of the hydrogen ion and the chlorine ion, giving rise to a quantum of $h\nu = eV$, where $V = 14 \cdot 0$ volts. The corresponding wave-length in the extreme ultraviolet is $\lambda = 880$ A.U., which could be observed, though with difficulty. A high voltage discharge through hydrogen chloride shows the ordinary spectrum of hydrogen. The attraction between a hydrogen nucleus and a halogen atom is about the same as the interaction between a hydrogen nucleus and the electron in the neutral hydrogen atom, as predicted by Haber. J. R. P.

Ionisation Potentials of Argon, Nitrogen, Carbon Monoxide, Helium, Hydrogen, and Mercury and Iodine Vapours. CLIFTON G. FOUND (*Physical Rev.*, 1920, **15**, 132—133).—The object was to determine the effect of gas on the volt-ampere characteristics of a two-electrode electron discharge tube, and to determine the voltage at which the gas affected the space charge of the tube or ionisation potential. By the use of a commutator, the heating circuit along the filament was broken while the space current was measured, so that the current, $i = A(V - V_0)^{3/2}$, where V_0 is the voltage equivalent to the initial velocity of the ions. The ionisation potential for argon was 15—16 volts at 1—200 bars pressure. With increase in filament temperature, due to the increased V_0, the potential was lowered. Nitrogen gave about 16 volts, carbon monoxide 13·5—14, mercury vapour 10—11, iodine vapour 8·5, whilst the values 20·5 for helium and 15 for hydrogen were uncertain. CHEMICAL ABSTRACTS.

Ionisation Potential of Mercury Vapour as a Function of the Temperature of the Cathode. T. C. HEBB (*Physical Rev.*, 1920, **15**, 130).—Values as low as 3·2 volts were obtained for the ionisation potential of mercury vapour at very high temperatures. The striking voltage, $V = 10 \cdot 5 - 0 \cdot 002T$, where T is the absolute temperature. CHEMICAL ABSTRACTS.

Ignition of Gases at Reduced Pressures by Transient Arcs. W. M. THORNTON (*Phil. Mag.*, 1920, [vi], **40**, 450—460).—The ignition of hydrogen, methane, ethane, pentane, propane, carbon monoxide, and coal gas by both direct- and alternating-current arcs has been investigated at a number of reduced pressures. The ignition current is plotted against the pressure, and curves produced in all cases. With direct-current arcs, the ignition current falls rapidly to a minimum with increase in pressure, and then rises equally rapidly to a maximum, after which it falls slowly to a constant value. The lower limit is found in all cases at about 0·2 atm., whilst the rapid rise lies between 0·4 and 0·5 atm. A mean ordinate (current in amperes) lies at the points:

hydrogen 0·30 ampere, methane 1·20 amperes, ethane 1·12 amperes, propane 0·87 ampere, and pentane 0·66 ampere, and these mean values may be expressed by the equation $i=0{\cdot}334+23{\cdot}5/\text{mol. wt.}$ The relative influence of hydrogen and carbon on the inflammability of the hydrocarbons is given by the equation

$$(i-i_0)=an_C/(n_H)^2,$$

where i is the ignition current of the hydrocarbon, i_0 that of hydrogen, a a constant, n_C and n_H, respectively, the number of carbon and hydrogen atoms. Two causes effect ignition, a thermal cause and an ionisation cause; either of these causes may be predominant, depending on conditions, and the form of the ignition curve depends on which of these causes is operative. With alternating current, the form of the curves is very much changed; in the case of hydrogen, the curve falls rapidly to 0·23 ampere, and then rises to 0·26 ampere, after which it falls to a steady value of about 0·1 ampere. With methane, there is only the slightest tendency for the curve to rise after the preliminary fall, but there is a halt, and then a slower fall to a stationary value. In the case of ethane and propane, the curve is of the same shape as that of methane, but the flat halt is very much longer. Coal gas is about ten times as inflammable as carbon monoxide. The whole of the curves given are reminiscent of the critical gas isothermal.

J. F. S.

Electrolysis of Solutions of Sodium Nitrite using a Silver Anode. F. H. JEFFERY (*Trans. Faraday Soc.*, 1920, **15**, 16—20).—The reactions at the anode during the electrolysis of solutions of sodium nitrite of different concentrations in a divided cell, with a silver anode and platinum cathode, were investigated. In no case was silver deposited on the cathode. Silver dissolved from the anode, no gas being evolved. A deposit formed on the anode, which was found to be silver nitrite, together with a small percentage of finely divided silver from the disintegration of the anode. Measurements of the anode potential were made, and the results showed that in the immediate neighbourhood of the anode the concentration of silver ions was not increased by the nitrate ions. A complex salt, $NaAg(NO_2)_2$, was isolated at the anode in small, well-shaped, bright yellow crystals by electrolysing an anolyte of 50 grams of sodium nitrite in 100 grams of water for fifty-five hours with a current of 0·072 ampere. The solution was allowed to evaporate isothermally over concentrated sulphuric acid in an exhausted desiccator. Further evaporation led to the separation of a mixture of this salt and sodium nitrite. J. R. P.

Transference Numbers of Sodium and Potassium in Mixed Chloride Solutions. S. A. BRALEY and J. LOWE HALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1770—1776).—Over a range of total concentration from $0{\cdot}2N$ to $1{\cdot}6N$ with equivalent amounts of sodium and potassium chlorides, a relatively greater amount of sodium is transferred than is indicated by calculation from the conductance of the simple salt solutions, on the basis of the iso-

hydric principle. The increase of sodium transferred over this range of concentration is, roughly, a linear function of the total salt concentration. The results are in harmony with those of Smith and Ball (A., 1917, ii, 247), and may be explained on the basis of complex formation, the simplest form of which may be expressed in the form $NaCl + KCl \rightleftarrows Na(KCl_2) \rightarrow Na^{\cdot} + KCl'_2$.

J. R. P.

Dependence of Electro-osmosis on the Chemical Properties of the Diaphragm. STANISLAW GLIXELLI (*Anzeiger Akad. Wiss. Krakau*, 1917, [*A*], 102—128; from *Chem. Zentr.*, 1920, iii, 431).—The fundamental assumption in the theory of electro-osmosis is that the potential of the mobile layer of liquid, ϕ_1, differs from the potential, ϕ_0, of the layer attached to the wall of the diaphragm. A proportionality exists between the difference of potential $(\phi_1 - \phi_0)$ of the electrical double layer and the rate of electro-osmosis or cataphoresis. The causes of the difference of potential and the mechanism of the phenomenon of the charge in the electrical double layer are discussed. All that is known is that the electrical double layer is considerably influenced by the addition of electrolytes, more particularly by hydrogen and multivalent ions and by the cations of the heavy metals and complex organic bases, and that the positively charged diaphragms are discharged by anions and the negatively charged ones by cations. The methods previously adopted have not permitted the use of moderately concentrated electrolytes. The author has elaborated a method of observing and approximately measuring the velocity of electro-osmosis which is particularly adapted to the estimation of the isoelectric point; it can be used with gels and powders, and permits the employment of approximately $0.5N$-solutions of electrolytes. The influence of hydrogen and hydroxyl ions on the electric charge of the following inorganic gels has been examined: silicic and tungstic acids, antimonic anhydride, stannic and titanic acids, glucinum oxide and hydroxide, zinc, iron, magnesium, and silver oxides, and nickel hydroxide. With some of these, the concentration of hydrogen and hydroxyl ions at the isoelectric point is determined; with others, the lower limit of its value is ascertained. With regard to the hydrogen-ion concentration at the isoelectric point, the substances examined fall into four distinct groups: acids, acid ampholytes, basic ampholytes, and bases. The results of the investigation are examined in the light of the present theories of the origin of the electric charge in colloid particles.

H. W.

Specific Heat of Liquids at Constant Volume. K. ZAKRZEWSKI (*Anzeiger Akad. Wiss. Krakau*, 1917, [*A*], 86—101; from *Chem. Zentr.*, 1920, iii, 440).—The values for $(\partial p/dt)_v = \alpha/\mu$ are calculated from the measurements of Seitz and Lechner (A., 1916, ii, 174). Whilst these values for ethyl alcohol at different temperatures between 0° and −90° lie with sufficient accuracy on a straight line in the $\partial p/\partial t$ volume diagram, for

ethyl ether and carbon disulphide they lie on different lines which are parallel to one another. Within this interval, $\partial^2 p/dt^2 = 0$ for alcohol, and therefore c_v is independent of the volume. For ether and carbon disulphide, on the other hand, $(\partial p/\partial t)_v = A + Bv$, in which A is a function of the temperature, and hence $\partial c_v/\partial_v = T\partial^2 p/J\partial t^2 = T\partial A/J\partial t$. Since the dependence of the specific heats, c_p, of these liquids on temperature has been investigated in this region by Battelli, it is possible to calculate c_v (for a mean volume, v). The following values for this factor are thus obtained:

	0°.	– 20°.	– 30°.	– 50°.	– 70°.	– 90°.
Ethyl alcohol...........	—	—	0·406	0·386	0·370	0·358
Ethyl ether	—	0·397	—	0·386	0·376	0·362
Carbon disulphide ...	0·160	0·139	—	0·121	0·114	0·110

A bend such as would be expected from the Planck-Einstein formula is only observed in the case of ether when c_v is plotted against the temperature; the opposite bend observed with alcohol and carbon disulphide is attributed by the author to the existence of complex molecules in these liquids. H. W.

Thermodynamics of Chemical Equilibrium in Condensed Mixtures. H. Cassel (*Zeitsch. Physik*, 1920, **2**, 71—75).—This is a straightforward thermodynamic argument, apparently proving rigorously, from Planck's statement of the third law, that any difference between the specific heats of the mixture and of the components separately, or any thermal effect on mixing, or any curvature in the vapour pressure isotherms, is a sign of chemical action. The effect of volume changes or deviations of the vapour from the gas laws is neglected, however. Chemical Abstracts.

Thermodynamic Properties of the Ions of some Strong Electrolytes and of the Hydrogen Ion in Solutions of Tenth-Molal Hydrochloric Acid containing Univalent Salts. Herbert S. Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1808—1832). —Measurements of the electromotive forces of the cells

$$H_2|MCl(c) \text{ in } HCl\ (0{\cdot}1)|HgCl|Hg$$

at 18°, 25°, and 30°, containing potassium, sodium, and lithium chlorides, respectively, have been made. Assuming the complete dissociation of the above electrolytes, it is shown that the hypothesis of the individual ion activities as postulated by MacInnes (A., 1919, ii, 385) is true within narrow limits, and that at a given concentration of potassium chloride the potassium and chlorine ion activities are identical within narrow limits. The individual ion activity-coefficients of the hydrogen, potassium, sodium, lithium, and chlorine ions from concentrations 0·1 to $3M$ have been calculated.

It is shown that the semi-empirical formula $\log F_a = ac - \beta c^m$, where F_a is the activity-coefficient of the ion, c the concentration, and a, β, and m are constants, will express F_a as a function of c within experimental error from 0·01 to $3M$ concentration. A table

of the free energies and heat content decreases of the cell reaction $H_2 + 2HgCl = 2HCl(0{\cdot}1) + 2Hg$ in the presence of potassium, sodium, and lithium chlorides, respectively, has been compiled.

On the assumption that the ions have independent heat contents of transfer, and that at a given concentration of potassium chloride the potassium and chlorine ions possess identical heat contents of transfer from a solution of concentration c_1 to a solution of concentration c_2, it is possible to calculate the decrease of heat content of transfer of the hydrogen ion from solutions of MCl(*c*) in HCl (0·1) to HCl (0·1). The results are tabulated. This decrease is shown to be a function of the total ion activity of the solution, not of the activity of the hydrogen ion. J. R. P.

Equation of State Covering all States of Aggregation and the Law of Action of the Molecules. LEON SCHAMES (*Zeitsch. Physik*, 1920, **1**, 376—384).—The author derives values for some of the constants of his equation. CHEMICAL ABSTRACTS.

Melting-point Methods at High Temperatures. LEO I. DANA and PAUL D. FOOTE (*Trans. Faraday Soc.*, 1920, **15**, 186—217).—Detailed descriptions are given of the methods of determining the melting points of metals, inorganic salts, and silicates by means of thermocouples, resistance thermometers, and optical pyrometers, as well as special methods. The following melting points are recorded: tin, 231·9°; bismuth, 271°; cadmium, 320·9°; lead, 327·4°; zinc, 419·4°; antimony, 630·0°; aluminium, 658·7°; silver, 960·5°; gold, 1063·0°; copper, 1083·0°; nickel, 1452°; cobalt, 1480°; iron, 1530°; palladium, 1550°; chromium, 1615°; platinum, 1755°; silicon, 1420°; sodium molybdate, 687°; borax, 741°; sodium chloride, 801°; sodium sulphate, 884°; sodium metasilicate (Na_2SiO_3), 1088°; lithium metasilicate, 1202°; lithium orthosilicate (Li_4SiO_4), 1255°, and various silicates, aluminates, and refractory materials. J. R. P.

The Relation between Boiling Point in the Vacuum of the Cathode Light and Critical Temperature. P. WALDEN (*Zeitsch. anorg. Chem.*, 1920, **112**, 225—232).—Making use of the data given by Krafft (A., 1896, ii, 464; 1899, ii, 464) for a number of paraffins, fatty acids and their esters, and benzene homologues of high molecular weight, it is shown that the ratio of the absolute boiling point, T_{15} at 15 mm., to that, T_0, in the vacuum of the cathode rays, has a mean value of 1·2. The ratio between the boiling points at 15 mm. and 760 mm. is given by $T_{15}/T_{760} = 0{\cdot}765$. It follows that $T_{760}/T_0 = 1{\cdot}59$, which is identical with the mean experimental value for the higher paraffins. This value is practically identical with that found by van Laar for the ratio of the critical temperature to the boiling temperature at atmospheric pressure, $T_k/T_{760} = 1{\cdot}60$. Hence the critical temperature is 2·54 times the boiling temperature in the highest vacuum. In the case of the metals potassium, sodium, silver, and copper, the relation between T_{760} and T_0 is expressed by $T_{760} = 4{\cdot}55T_0/\log T_0$.

The above relation between critical temperature and boiling points is applied to calculate the critical temperature of metals. For those metals of which the boiling point in absolute vacuum is not known, this is calculated from the relation that $T_0/T_{vap.} = 1{\cdot}8$, where $T_{vap.}$ is the temperature at which vaporisation begins in the vacuum of the cathode rays. E. H. R.

Direct Measurement of the Thermal Molecular Velocity. OTTO STERN (*Zeitsch. Physik*, 1920, **2**, 49—56).—A silvered platinum wire is electrically heated in a high vacuum (0·0001 mm. Hg) until silver molecules leave it with a mean free path greater than the length of the containing vessel. Those of a certain direction are selected by passing two slits 0·2 mm. wide, and next strike a brass screen 10 cm. away, where they condense as a dark line. If the apparatus is rotated, the line is displaced by an amount from which the velocity of the molecules can be calculated. The speed of rotation was 1500 rev. per minute, and the displacement about 4 mm. The indirectly known value was confirmed to 15%, about the uncertainty due to imperfect knowledge of the temperature. The molecule of gaseous silver was shown to be monatomic. CHEMICAL ABSTRACTS.

Determination of Vapour Pressure. E. J. HARTUNG (*Trans. Faraday Soc.*, 1920, **15**, 150—159).—An improved tensimeter is described, which allows of the determination of vapour pressures with great accuracy. The vapour pressures at 0° of solutions of potassium chloride, potassium sulphate, and sulphuric acid were compared with that of a solution of potassium chloride saturated at 0°. J. R. P.

Vapour Pressure of Aqueous Solutions of Mannitol. J. C. W. FRAZER, B. F. LOVELACE, and T. H. ROGERS (*J. Amer. Chem. Soc.*, 1920, **42**, 1793—1808).—The vapour pressure lowerings of aqueous mannitol solutions have been determined over the range of solubility of the substance. The error due to dissolved air was eliminated. A mean deviation from Raoult's law of only 0·0006 mm. was found up to 0·8 molar concentration. By comparison with freezing-point lowerings, it is found that $\log_e p_0/p_1$ decreases with the temperature, or the heat of dilution has a small negative value for concentrations up to 0·5 molar. Comparisons with boiling-point determinations show that this changes to a positive value at higher concentrations. J. R. P.

Thermochemistry of Ionisation of Vapours of certain Compounds. PAUL D. FOOTE and F. L. MOHLER (*J. Washington Acad. Sci.*, 1920, **10**, 435—444).—If a material in the vapour state ionises by dissociation it is sometimes possible to calculate the ionisation potential from chemical and physical data. In the case of alkali-metal haloids, all the necessary data are known except the heat of sublimation. The heat of sublimation may be calculated

for haloids of metals of the second group from the vapour pressures. The ionisation potentials are computed for hydrogen chloride, bromide, iodide and sulphide, and the value for hydrogen chloride is found to be in agreement with the number determined by the authors. J. R. P.

Thermochemistry of Carbon Compounds. A. THIEL (*Ber.*, 1920, **53**, [*B*], 1378—1382).—A criticism of the work of Fajans (this vol., ii, 354) and von Steiger (this vol., ii, 355). The author considers that Fajans' calculations are to some extent based on fundamentally invalid assumptions. For example, the existence of monatomic carbon vapour is assumed into which carbon could only dissociate to the extent of about 50% at 10,000° according to calculations based on the theory itself. It is further assumed that the atoms in the crystal lattice of diamond are united to one another by the same valencies as in aliphatic compounds. In general, however, this can scarcely be the case, since it would then be impossible to explain the crystalline form of elements of lower valency; in all probability, only subsidiary valencies can be involved. H. W.

The Benzene [Formula] Problem. III. A. VON WEINBERG (*Ber.*, 1920, **53**, [*B*], 1353—1358).—As a result of recent experiments, Debye and Scherrer (A., 1917, ii, 437) have been led to the conclusion that carbon in the form of diamond is to be regarded as the prototype of aliphatic compounds, whilst graphite and amorphous carbon are the simplest stages in aromatic chemistry. The author does not regard the production of mellitic acid from graphite (and not from diamond) as valid evidence of aromatic nature, since it is not a primary product. Further, Debye and Scherrer have seen in the suppressed fourth valency of the carbon atoms in benzene an analogy to the mechanically suppressible fourth valency of the graphitic carbon atom, and point to the behaviour of the triarylmethyls as proof of the existence of such weakened fourth valencies; in reality, however, the valency is not weakened, as is evidenced by the behaviour of this class of substance towards oxygen, but only intermittently saturated in consequence of the induced vibrations of the central carbon atom. Von Steiger (this vol., ii, 355) has adduced evidence in favour of Debye and Scherrer's hypothesis by consideration of the heats of combustion of aromatic compounds. It is shown, however, that the energy involved in the isolation and combustion of a carbon atom in benzene is 5·3 Cal. greater than that involved in the case of an aliphatic hydrocarbon and 7 Cal. greater than that involved with graphite. It therefore appears that benzene rings cannot be present in graphite, and, more generally, that it represents a particular type of union. The kinetic formula for benzene leads to the hypothesis that the excess of energy (5·3 Cal.) for an aromatic in comparison with an aliphatic carbon atom is a consequence of its more rapid movement, and is the logical conclusion of the theory that the energy excess of

multiple bonds is kinetic in origin—a theory which is defended by examples against the criticisms of Fajans. H. W.

Heats of Combustion and Energy of Dissociation. I. A. von Weinberg (*Ber.*, 1920, **53**, [*B*], 1347—1353).—The present communication contains a concise statement and justification of the views previously expressed in part by the author (this vol., ii, 14) and more recently criticised in some particulars by Fajans (this vol., ii, 354). They may be expressed in the following manner: (1) in saturated aliphatic hydrocarbons, the energy of dissociation of a C–C bond is equal to that of a C–H bond, that is, $Q_{CC}=Q_{CH}$; (2) the absolute value of Q_{CH} is 7·5 Cal. greater than the energy of dissociation of a hydrogen molecule; (3) molecular cohesive forces have not to be overcome in the combustion of solid carbon, which practically only requires the provision of the energy of four C valencies for the carbon atom. The absolute value for diamond or graphite is $2Q_{CC}+1·5$ Cal. (4) In the oxidation of carbon monoxide to carbon dioxide the energy of dissociation of the two so-called unsaturated valencies is equal to Q_{CC}.

(1) If it be admitted that the energy required for the separation of two similar or dissimilar atoms is evenly distributed between the atoms, the following expression is obtained for the energy of disruption of a hydrocarbon, $C_nH_{2n+2}-[(n-1)Q_{CC}+2n+2/2\,.\,Q_{CH}]-[2n+2/2\,.\,Q_{CH}]$, in which the left bracket represents the energy required for the separation of n carbon atoms and the right bracket that required for $2n+2$ hydrogen atoms. The contribution of the n carbon atoms towards the heat of combustion of the hydrocarbon is $nx=-[(n-1)Q_{CC}+(n+1)Q_{CH}]+nQ_{CO_2}-nQ_{O_2}$, where Q_{CO_2} and Q_{O_2} are the energies of dissociation of carbon dioxide and oxygen. The summation law demands that this shall be true for any value of n, which can only be the case when $Q_{CC}=Q_{CH}$. (2) The values for the energy of dissociation of a hydrogen molecule are calculated from the recent experiments of Franck, Knipping, and Krüger. It is at present impossible to elucidate the intramolecular process on which the difference depends. (3) If 96 Cal. be adopted as the most probable value for the heat of combustion of solid amorphous carbon, it appears that the latter behaves during combustion as a gaseous saturated hydrocarbon. Solid carbon therefore occupies a position different from that of all solid organic compounds, and it appears justifiable to conclude that liquid molecular carbon is incapable of existence. The heat of combustion of diamond has been determined with great accuracy to be 94·5 Cal., and this difference of 1·5 Cal. can only be explained on the supposition that the work of dissociation in diamond is correspondingly greater. (4) Thomsen has already endeavoured to calculate the absolute value for the energy of dissociation of a carbon atom from solid carbon by consideration of the oxidations of the element to carbon monoxide and dioxide respectively, but the author holds this mode of reasoning to be incorrect, since it assumes the similarity of the C–O double bond in carbon monoxide and the two C–O linkings in carbon dioxide.

He prefers to calculate Q_{CO} from the heats of combustion of a number of aldehydes and ketones, and thus deduces the value 66·7 Cal. (the value may be slightly inaccurate on account of the experimental difficulties in working with the more volatile substances); the mean value of the heat of combustion of carbon monoxide as determined by Berthelot and Thomsen is 67·4 Cal., a figure which agrees with the former within the limits of experimental error. It follows, therefore, that the two so-called unsaturated valencies of carbon monoxide are not free during combustion, but require as much energy for their separation as does the carbonyl group of a ketone. It therefore seems probable that the four carbon valencies in carbon monoxide are attached to the oxygen atom. H. W.

Heats of Combustion and Energy of Dissociation. II. A. VON WEINBERG (*Ber.*, 1920, **53**, [*B*], 1519—1528).—On the basis of the ideas developed in previous communications (this vol., ii, 14, and preceding abstract), the author has calculated the energy necessary for the fission of the commoner atomic linkings in organic compounds. In the following, the energy of dissociation is represented by Q, and the index shows the linking concerned.

It is found that $Q_{CC}=Q_{CH}=Q_{C-O}=Q_{NH}=Q_{N-N}$, or that five of the commonest linkings in organic compounds are almost equally stable at 18°. The elimination of the first oxygen atom from carbon dioxide requires an expenditure of energy equal to 126·7 Cal., whilst for the second oxygen atom 265·5 Cal. (approximately double that used in the former case) are necessary. $Q_{O\cdot H}$ in ethyl alcohol and ethylene glycol is calculated to be 96·8 and 98·7 Cal. respectively, whilst in water it is 99·2 Cal.; the difference lies within the limits of experimental error, but it is quite possible that the OH linking in alcohols is slightly less stable than in water. The values calculated for $Q_{N\equiv N}$ and Q_{NC} are 266·4 Cal. and 233·1 Cal.; from this it follows that the treble bond in the case of nitrogen, in contrast to that of carbon, is exactly equivalent to three single bonds, and this explains why substances containing the group $C\equiv N$ or $N\equiv N$ are not possessed of the same lability and power of forming additive compounds as are those containing the C:C group. Q_{NO} and Q_{NO_2} are 170·9 Cal. and 243·7 Cal. respectively. Q_{HCl} is calculated to 119·2 Cal., which is in good agreement with the value (119 Cal.) found by Born (this vol., ii, 156) by a totally different method, and thus strikingly confirming Born and Haber's prediction that the energy of dissociation, Q_{HCl}, is equal to the electronic affinity of the chlorine atom. Q_{CCl} is calculated to be 119·6 Cal., so that practically the same expenditure of energy is necessary to separate the hydrogen nucleus from the electron, the hydrogen atom from the chlorine atom, and the latter from the carbon atom. Q_{Cl-O}, Q_{HBr}, Q_{CBr}, Q_{HI} and Q_{CI} are 78·8, 76·3, 74·2, 59·4, and 54·5 Cal. respectively, so that bromine and iodine are rather more firmly combined with hydrogen than with carbon. The equality of energy of dissociation and electronic affinity is not found with bromine and iodine. The difference between the energy of the corresponding linkings explains the differ-

ences in the reactivity of the alkyl haloids. Q_{S_2} is calculated to be 104·5 Cal., which is in good agreement with the value (103·6 Cal.) determined experimentally by Budde. Q_{SO_2} and Q_{SO_3} are respectively 254·5 Cal. and 336·2 Cal.; Q_{CS} and Q_{H_2S} are 73·1 Cal. and 152·8 Cal. respectively (the latter value differing widely from that calculated by Born). For Q_{SCl} the values 76·4 Cal. and 71·2 Cal. are calculated from different compounds. H. W.

Heat of Oxidation of Glucinum. H. COPAUX and CH. PHILIPS (*Compt. rend.*, 1920, **171**, 630—632).—From measurements of the heat of solution of glucinum and its oxide respectively in hydrofluoric acid the author calculates the heat of oxidation of glucinum to be given by $Gl_{sol.} + O_{gas} = GlO_{sol.} + 151·5$ cal. W. G.

Physico-chemical Properties of Highly Concentrated Dispersoidal Solutions of Noble Metals. N. I. MOROSOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 783).—The viscosity of a 17·7% silver solution at 19·5° is 1·1129 times that of water. The viscosity decreases with increasing temperature, for example, the time of flow for 17·7% silver solution at 19·5° is 49·7 sec. and at 34·5°, 37 sec. The study of dispersoidal solutions (viscosity, b. p., etc.) of high concentrations undoubtedly will make possible a qualitative correlation among the degree of dispersity, the concentration of disperse phase and changes of properties of the disperse medium.

CHEMICAL ABSTRACTS.

The Viscosity of Liquids. IV. Ideal Mixtures of the Types Ether-Ether and Ester-Ester. JAMES KENDALL and ALEXANDER HOLLAND WRIGHT (*J. Amer. Chem. Soc.*, 1920, **42**, 1776—1784. Compare A., 1914, ii, 109; 1917, ii, 524, 525).—The viscosity curves for the following liquid systems have been determined with the use of the Bingham viscosimeter: (1) ethyl ether–phenetole; (2) ethyl ether–diphenyl ether; (3) phenetole–diphenyl ether; (4) ethyl acetate–ethyl benzoate; (5) ethyl acetate–benzyl benzoate; (6) ethyl benzoate–benzyl benzoate. Although these mixtures are certainly very nearly ideal, yet the experimental data are not reproducible satisfactorily by means of any known simple formula. The logarithmic viscosity formula of Arrhenius gives values uniformly a little low; the cube root viscosity equation of Kendall and Monroe (*loc. cit.*) gives values uniformly a little high. All other proposed formulæ are altogether out of agreement with the figures of experiment. It is concluded that the experimental work has advanced as far as possible, and that further progress must be preceded by fundamental advances in the theory of the subject.

J. R. P.

The Influence of Temperature on the Surface Tension of Narcotics. HANS WINTERSTEIN [with (FRL.) ELSE HIRSCHBERG] (*Biochem. Zeitsch.*, 1919, **100**, 81—83).—The surface activity of benzamide, monacetin, salicylamide, and ethyl urethane increases with a rise in temperature. S. S. Z.

The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. II. EDWARD BRADFORD MAXTED (T., 1920, **117**, 1280—1288).

Adsorption from Solutions of Substances of Limited Solubility. M. POLÁNYI (*Zeitsch. Physik*, 1920, **2**, 111—116).—A mathematical paper. CHEMICAL ABSTRACTS.

Mechanism of the Surface Phenomena of Flotation. IRVING LANGMUIR (*Trans. Faraday Soc.*, 1920, **16**, 62—74).—The adsorption of organic substances with large molecules originates from certain atoms in the molecule. Wetting is due to the attraction between the material wetted and some active group in the liquid molecule. A study of cleaned and oiled glass surfaces showed that films of molecular thickness are sufficient to alter radically the surfaces of solids, both as regards the lubricating properties of these films and the contact angles made by water drops. The formation of froth depends on the presence of substances which can form a stable unimolecular film over the surface of each bubble. In order that a froth may readily form, it seems desirable to have present a soluble substance having a strong tendency to be adsorbed on the surface of the liquid. The presence of alkalis in flotation is to be avoided, probably because the hydroxyl ion tends to draw the carboxyl group of the fatty acid to itself rather than allow it to attach itself to the solid particles. The tendency of particles to attach themselves to bubbles of the froth is measured by the contact angle formed between the oily surface of the bubble and the contaminated surface of the solid. The selective action by which substances like galena are separated from quartz and calcite is dependent on the contact angle formed by the oiled surfaces rather than on any selective tendency for the oil to be taken up by some minerals more than by others. J. R. P.

The Diffusion of Electrolytes into Jellies. III. The Relation of the Distance of Diffusion to the Diffusion Coefficient and its Dependence on the Concentration of the Indicators. OTTO FÜRTH, HANS BAUER, and HANSI PIESCH (*Biochem. Zeitsch.*, 1919, **100**, 29—64. See A., 1919, ii, 13; this vol., ii, 94).—The diffusion of various electrolytes in agar jellies was studied, and it was found that the laws of diffusion could also mostly be applied to diffusion into jellies. It was further found that the "invasion factor," that is, the relation of the distance of diffusion of the electrolyte in question to that of a sodium chloride solution of the same molecular concentration diffusing under the same conditions, was an approximate measure for the square root of the diffusion-coefficient. It is concluded from this that most electrolytes also penetrate jellies according to the mobility of their ions providing that chemical affinity and colloidal changes do not interfere. The

distance of diffusion is influenced by the concentration of the indicator in the jellies. S. S. Z.

The Effect of Asymmetry. A Study in Crystal Structure. THOMAS VIPOND BARKER and MARY WINEARLS PORTER (T., 1920, **117**, 1303—1321).

The Electrochemical Behaviour of Mixed Crystals of Gold with Copper and Silver. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **112**, 233—243).—In previous papers (A., 1919, ii, 398, 406) it has been shown that there is a limiting composition for gold–copper and gold–silver alloys, such that, when the gold content exceeds this limit, the alloys are not attacked by different chemical reagents. The limiting composition was correlated with the probable distribution of the two kinds of atom on a face-centred cubic lattice in the crystalline structure of the alloy. The electrochemical properties of these alloys have now been investigated. When copper–gold alloys are used as anode in an electrolytic cell, with a copper cathode and copper sulphate or nitrate as electrolyte, the limiting composition is about 0·27 to 0·30 mol. of gold; with a smaller proportion of gold than this, copper is dissolved from the anode. With gold–silver alloys as anode, using sulphuric or nitric acid as electrolyte, the limiting composition is 0·35 to 0·40 mol. of gold. Similar limits were found when the decomposition potentials of such cells were measured. On the other hand, to obtain a persistent polarisation effect of 1·4 volts in the case of gold–copper and 0·73 volt for gold–silver, the proportion of gold to silver or copper must not fall below 0·5 mol. The normal limiting composition for weak oxidising agents, such as hydrogen peroxide, in acid or alkaline solution is about 0·25 mol. of gold; in the case of anodic oxygen, therefore, this normal limit is exceeded. The same is true of anodic sulphur, produced by the electrolysis of sodium sulphide, the limit in this case being more than 0·50 mol. of gold.

Discussing these observations from the point of view of the space-lattice theory, the author points out that in an alloy containing 0·25 mol. of gold, that is, 1 atom of gold to 3 of copper, in the face-centred cubic lattice there will not be in any cube face plane any two copper atoms the distance of which from one another corresponds with the minimum translation in the lattice. The alloy would therefore be protected against attack by any agent which needs two atoms of copper. If the agent can attack the copper, on the other planes, but the gold atoms retain their positions, then, if the agent cannot penetrate the structure, the alloy is still resistant.

The limiting composition for strong anodic polarisation of the alloys, 0·5 mol. gold, is the same as the limiting composition in gold–palladium alloys for hydrogen solubility. These facts may be correlated with the presence in the structure of alloys containing 0·5 mol. of gold or less of cube edges or diagonals formed exclusively of copper or silver or palladium atoms. E. H. R.

Relation between the Solubilities of Solutes and their Molecular Volumes. SHINKICHI HORIBA (*Trans. Faraday Soc.*, 1920, **15**, 178—185).—When a solute of molecular volume V is dissolved in a solvent of molecular volume v, the number of molecules of solvent which can surround one solute molecule is approximately $4/1{\cdot}1\,.\,(\sqrt[3]{V/v}+1)^2$, assuming that V is distinctly larger than v. If the logarithms of the solubilities are plotted against this expression, straight lines are obtained. J. R. P.

Mutual Action of Trimethylsulphanilic Acid and Strong Electrolytes. MASAO KATAYAMA and NOBUO YAMADA (*J. Tokyo Chem. Soc.*, 1920, **41**, 193—224).—It has been shown (*ibid.*, **36**, 745) that trimethylsulphanilic acid is not an electrolyte, but lowers the electrical conductivity of other electrolytes, due either to interference of ionic velocity of the electrolytes or to formation of complex salts. The authors failed to obtain the crystalline complex salts reported by Griess (A., 1880, 322), except when potassium salts were present. The complex salts prepared by Griess, therefore, must have either contained potassium salts or methylation must have been incomplete. From determinations of the transport number of hydrochloric acid containing the sulphonic acid, it is shown that there is no complex salt formation. Viscosity measurements of aqueous solutions of trimethylsulphanilic, hydrochloric, and acetic acids show that the effect is additive for acetic acid and the sulphonic acid, but is not so for hydrochloric acid and the sulphonic acid. The change of conductivity of both hydrochloric and acetic acids produced by the addition of the sulphonic acid is entirely due to the change of viscosity. The solubility and the change of volume produced when the sulphonic acid is added to water, hydrochloric acid, and acetic acid are also measured. The general conclusion is that hydrochloric acid increases the dissociation of trimethylsulphanilic acid, but the latter does not affect the dissociation of hydrochloric acid. CHEMICAL ABSTRACTS.

Reversible and Irreversible Dispersoidal Parasitism. P. P. VON WEIMARN, N. I. MOROSOV, and V. J. ANOSSOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 782).—An investigation on the conditions of formation of dry and solid preparations of silver, which are reversibly soluble, leads to the following conclusions: Dispersoidal parasitism is reversible in the limits of ordinary temperature (20—25°) only when the substance which originates it is soluble at these temperatures. Examples: silver + gum, silver + dextrin. Dispersoidal parasitism is irreversible in the limits of the ordinary temperature if the substance which originates it is insoluble at these temperatures. Examples: silver + agar, silver + gelatin. Gelatin and agar are therefore stabilisers only for liquid preparations of dispersoidal silver, and the dried preparations do not dissolve in water at 20—25°. A method has been developed for obtaining liquid solutions of silver of very high dispersity; concentrations of 15% and more are easily obtainable in about one hour. CHEMICAL ABSTRACTS.

Method of obtaining Dry Precipitates of any Insoluble Substances, which pass into Dispersoidal-dissolved State Commencing only from some Fixed Temperatures. P. P. von Weimarn, N. I. Morosov, and V. J. Anossov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 197).—Dispersoidal parasitism is characterised by the fact that any insoluble substance (for example, silver, sulphur, barium sulphate, etc.) receives nearly the same properties of "solubility" as a substance at the expense of which it parasites. Therefore, by mixing together any insoluble precipitate of high dispersity with various substances which are parasitised and which are sufficiently soluble, for example, successively at 10°, 20°, 30°, 40°, etc., there is obtained a succession of dry preparations of the insoluble substance. These preparations are "soluble" also successively in the vicinity of temperatures enumerated above. Many organic substances (solutoids, for example, gelatin), on heating of their solutions for a long time, give products soluble at still lower temperatures than the original substance. These temperatures are lower the longer the solution is heated. These products are especially convenient for realisation of the method here described. For example, a dry precipitate of dispersoidal silver (63% of Ag) which is prepared with gelatin, previously boiled for seven hours, practically "does not dissolve" in water at about 20°, but it "dissolves" excellently at about 35°, giving very stable silver "solutions" of high dispersity. Chemical Abstracts.

Coagulation of Agar-agar Hydrosol. Keizo Iwase (*J. Tokyo Chem. Soc.*, 1920, **41**, 468—479).—The effects of temperature and of salts on the velocity of coagulation were studied. Agar-agar was washed with dilute acetic acid, water, aqueous ammonia, and water, dissolved by heat, and then filtered. The precipitate produced by alcohol, and dried with alcohol and ether, was a white powder. A known concentration of agar-agar was prepared by dissolving this powder and heating under a reflux condenser. The hydrosol thus obtained was transferred to test-tubes and kept in a bath 20° higher than the temperature under which experiments were to be conducted. The end-point of the coagulation was taken at the time when the agar not only would not flow, but also its surface meniscus could not be disturbed on inverting the test-tube. The general conclusions are: The more concentrated the hydrosol, the greater is the speed of coagulation. The effect of the salts on coagulation time is greater when the hydrosol is the more concentrated. Series of ionic effect are $K > Na_2SO_4 > CH_3 \cdot COO > C_6H_4O_5 > Cl > Br > NO_3 > I$. Although the temperature effect on the speed of coagulation is very great, the order of this series of the salt effect at different temperatures does not change. The heating of the sol prolongs the time of coagulation, finally rendering it non-coagulable. Chemical Abstracts.

Sedimentation. Peter Rona and Paul György (*Biochem. Zeitsch.*, 1920, **105**, 133—140).—According to Bodländer (*Jahrb. Min.*, 1893, **2**, 147), small proportions of electrolytes

soluble in water cause rapid clarification of kaolin suspensions, whereas soluble non-electrolytes, even in large amounts, are ineffective in this respect (compare Kruyt and van Duin, A., 1914, ii, 182; Freundlich and Rona, A., 1917, ii, 365; Rona and Michaelis, A., 1919, ii, 269). The authors have now made further experiments with methyl, ethyl, *iso*propyl, amyl, heptyl, *n*- and *sec*.-octyl, and decyl alcohols, methyl-, ethyl-, propyl-, *iso*butyl-, and phenyl-urethanes, diphenylthiocarbamide, chloroform, tributyrin, camphor, and thymol, and find that nearly all of these non-electrolytes increase the velocity of sedimentation of kaolin. In homologous series, this acceleration increases in magnitude with the length of the chain, and only with compounds virtually insoluble in water is no effect detectable.

The increases in the viscosity of water produced by these compounds are at most very small, and the authors assume that the non-electrolytes produce a sensibilisation of the suspended particles towards the electrolytes always present, and thus increase the velocity of sedimentation of the kaolin particles. This view is supported by the observation that the velocity of sedimentation of charcoal is not influenced by non-electrolytes. T. H. P.

Structure of Precipitates. SVEN ODÉN (*Svensk. Kem. Tidskr.*, 1920, **32**, 90—98; from *Chem. Zentr.*, 1920, iii, 326—327. Compare this vol., ii, 600).—The author has endeavoured to develop a theory concerning disaggregation and aggregation with increasing electrolyte content, but the subject is difficult, on account of the limited knowledge regarding the electrical double layer. Freundler's absorption formula may be adopted, and the assumption may be made that for each type of ion a special adsorption isotherm of the form $y=\beta c^a$ exists in which the coefficient is greater for one variety of ion and the exponent greater for the other. The derived relationships are expressed by graphs. The author considers that the so-called peptisation of a precipitate consists exclusively in the adsorption of ions, with discharge of the primary particles and subsequent scattering of the aggregates. The influence of concentration, temperature, and rate of admixture of the reacting solutions on the size of the primary particles has been accurately investigated. The effect of concentration on the structure of precipitated barium sulphate has been examined with solutions of barium thiocyanate and ammonium sulphate. If the concentration of the supersaturated barium sulphate solution at the moment when primary particles separate be denoted by M, it appears that, with diminishing concentration of the reacting solutions, the primary particles are of sufficient size to remain stable when $M=0{\cdot}25$. The distribution curves for the magnitudes of the particles are given. If one solution is added drop by drop to the other, the barium sulphate primarily formed separates at a considerably lower value of M, and consequently in correspondingly larger particles than if the total quantity of barium sulphate is simultaneously produced. The influence of rate of addition on the primary structure is quantitatively examined with the help of

solutions of barium nitrate and ammonium sulphate, and the results are given in a series of graphs. Finally, the effect of temperature is studied, and the well-known phenomenon that precipitated barium sulphate becomes coarser with increasing temperature is quantitatively examined. H. W.

Copper Ferrocyanide. E. J. HARTUNG (*Trans. Faraday Soc.*, 1920, **15**, 160—177).—Preliminary experiments on the equilibrium between moist copper ferrocyanide and aqueous vapour, and on the adsorption of potassium chloride and potassium sulphate from solutions by copper ferrocyanide, are described. The function of copper ferrocyanide in semi-permeable membranes is discussed.
J. R. P.

Equation for the Chemical Equilibrium of Homogeneous Mixtures. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1920, **15**, 75—82).—A mathematical paper in which the conditions for the equilibrium of a homogeneous mixture at constant temperature, and the effect of pressure on the equilibrium constant, are deduced by rigorous methods. J. R. P.

Self-ignition of Ethyl Ether–Air Mixtures. J. A. MCCLELLAND and H. V. GILL (*Sci. Proc. Roy. Dublin Soc.*, 1920, [N.S.], **16**, 109—119).—Ignition occurs when a mixture of ethyl ether vapour and air is allowed to rush into a partly exhausted tube. Measurements of the temperature in the tube showed that the rise of temperature produced reached the ignition point of the mixture. The rise of temperature is attributed to the conversion into heat of the translational energy of the gas rushing into the tube. The length of the explosion tube affects the results. J. R. P.

Theory of Velocity of Reaction. M. POLÁNYI (*Zeitsch. Physik*, 1920, **2**, 90—110. Compare this vol., ii, 238).—The non-mechanical nature of chemical processes, considered in conjunction with the quantum hypothesis, leads to the conclusion that chemical decomposition is influenced by atomic vibrations. It is assumed that these vibrations are irregular. Formulæ have been deduced for the reaction velocity of different types of chemical processes. CHEMICAL ABSTRACTS.

Velocity of Unimolecular Reactions. ERIC K. RIDEAL (*Phil. Mag.*, 1920, [vi], **40**, 461—465).—A theoretical paper in which unimolecular reactions are considered from the point of view of the radiation hypothesis. It is shown that the reaction velocity of a unimolecular reaction is given by the expression $dn/dt = \nu \, . \, e^{-h\nu/kT}$, where ν, the activating radiation frequency, is identical with the time of molecular relaxation. On the basis of the radiation theory, light would appear to be corpuscular, the size

of a quantum being equal to a wave-length of light. If its energy be due to an electrostatic charge, E, then $E^2=2hc$. J. F. S.

The Propagation of Flame in Mixtures of Methane and Air. II. Vertical Propagation. III. Propagation in Currents of the Mixtures. WALTER MASON and RICHARD VERNON WHEELER (T., 1920, **117**, 1227—1240).

Kinetics of the Reaction of Nitrous Acid, particularly towards Halogen Oxyacids. ALBIN KURTENACKER (*Monatsh.*, 1920, **41**, 91—113. Compare A., 1914, ii, 552; 1915, ii, 537, 622). —The action of sodium nitrite in aqueous solution towards potassium chlorate, dichromate, and permanganate in the presence of potassium hydrogen sulphate has been kinetically investigated. With the first two oxidising agents, the solutions of sodium nitrite and potassium hydrogen sulphate are mixed at 20°, and, after a period of about fifteen minutes, during which the solution acquires a steady condition, the agent is added. Aliquot portions of the mixture are removed at definite intervals and almost neutralised by alkali; the nitrous acid is destroyed by protracted ebullition with ammonium sulphate, and the unchanged oxidising agent is estimated by the addition of a measured volume of ferrous sulphate solution, followed by titration of the excess of the latter with $N/10$-permanganate solution. In the case of potassium permanganate, reaction proceeds very rapidly, even in dilute solution, and the measurements are effected by noting the time necessary for the decolorisation of a known quantity of permanganate by potassium nitrite in the presence of acetic acid.

The chlorate–nitrite reaction can be expressed by the formula $dx/dt=[K_1+K_2S](ClO_3')(HNO_2)$, where K_1 is the velocity-coefficient of the uncatalysed action, K_2 the acceleration-coefficient of the acid, and S the concentration of the latter, whilst with dichromate the expression becomes

$$dx/dt=[K_1+K_2(S)^2](H_2Cr_2O_7)(HNO_2).$$

In all probability it is the undissociated nitrous acid, and not the nitrite ion, which takes part in the change. Similarly, the catalytically accelerating action of the added acid

$$(KHSO_4,CH_3\cdot CO_2H)$$

is probably to be attributed to the undissociated molecules (or HSO_4' ions), and not to the hydrogen ions. The independence of the rate of reaction of the concentration of the nitrite, which is a feature of the bromate reaction, is not observed in any of the new cases under investigation. Very marked differences are found in the mechanism of the action of chloric, bromic, and iodic acids respectively; the greatest abnormality is observed with bromic acid, which, in contrast with its position in the natural series, acts much more rapidly than either chloric or iodic acid. Further experiments with other oxidising agents will be necessary to elucidate the reasons of this divergent behaviour. Permanganate reacts

much more rapidly with nitrous acid than does any other oxidising agent. H. W.

Comparative Rate of Hydrolysis of the Fatty Esters of Different Alcohols. H. HEINRICH FRANCK (*Seifenfabr.*, 1920, **40**, 293—294; from *Chem. Zentr.*, 1920, iii, 337).—In order to investigate the relationship between resorption and rate of hydrolysis of fatty esters, the author has determined the latter factor for linseed oil and for the ethyl and ethylene esters of the fatty acids of this oil. The substances were dissolved in light petroleum and treated with alcoholic-potassium hydroxide solution at 34° or 4°, the free acid being periodically tested. Differences in the rates of hydrolysis were not great, the glyceryl ester being most rapidly, and the ethyl ester least readily, affected. With esters of the polyhydroxy-alcohols, the curves showing the rate of hydrolysis indicate a primary rise followed by a distinct minimum, which is apparently due to temporary formation of the ethyl ester. Enzymic fission by "steapsin Grübler" was also investigated, and the curves again show a minimum after an initial maximum. In agreement with other experiments, the order glyceryl, ethyl, ethylene ester is established. H. W.

The Hydrolysis of Platinum Salts. I. Potassium Platinichloride. EBEN HENRY ARCHIBALD (T., 1920, **117**, 1104—1120).

Significance of Neutral Salts as Catalysts in Chemical Reactions. OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1920, **106**, 134—138).—The author confirms the observation of Wurster (A., 1889, 1242) that hydrogen peroxide and a solution of α-naphthylamine in dilute acetic acid react, with formation of a colouring matter, in presence of sodium chloride. It is found that this reaction takes place instantaneously in presence of lithium chloride, almost as quickly with magnesium, calcium, or aluminium chloride, and only after the lapse of several minutes with sodium, ammonium, or potassium chloride. The sulphates and nitrates corresponding with these chlorides are inactive in this respect, as also are potassium sodium tartrate and potassium citrate and acetate. In place of α-naphthylamine, any other readily oxidisable aromatic amine may be employed, but β-naphthylamine does not respond to the reaction. The pronounced effect produced by lithium chloride is doubtless due to the stronger secondary valencies of the lithium in comparison with those of sodium and potassium, the aromatic amine to be oxidised first undergoing loose union with the central lithium atom. The oxidation of aniline salts or of benzidine by means of sodium ammonioprusside in presence of atmospheric oxygen or hydrogen peroxide does not seem to differ fundamentally from the oxidation of aniline acetate by means of hydrogen peroxide in presence of lithium chloride. The well-known oxidation of ammonia to nitrous acid by the agency of

copper hydroxide and atmospheric oxygen is probably of the same character; just as in the oxidation of ammonia by hydrogen peroxide in presence of sodium chloride, the ammonia first enters into co-ordinative union with the central metallic atom, oxidation to nitrous acid by the activated oxygen then occurring readily.

T. H. P.

Studies in Catalysis. XIV. The Mechanism of the Inversion of Sucrose. CATHERINE MARGARET JONES and WILLIAM CUDMORE McCULLAGH LEWIS (T., 1920, **117**, 1120—1133).

Catalysis in the Hydrolysis of Esters by Infra-red Radiation. ERIC KEIGHTLEY RIDEAL and JAMES ARTHUR HAWKINS (T., 1920, **117**, 1288—1296).

Origin of the Elements. J. H. VINCENT (*Proc. Physical Soc. London*, 1920, **32**, 271—290).—A theoretical paper in which hypotheses in connexion with the origin of the elements are put forward. The atomic weights are regarded as the weighted mean values of the atomic weights of the isotopes of the elements, but it is assumed that, as a rule, the atomic weight of the ordinarily occurring element is near to that of some one isotope. Figures and tables are drawn up showing how this accounts for the accepted values of a large number of atomic weights, if it is also assumed that the weights and positions in the periodic table of any isotope are conditioned by laws similar to those holding in the recognised radioactive families. The elements are all supposed to be derived from parent elements by processes known to occur in actively radiating families, but their radioactivity is not, in general, detectable by the usual means, owing to the velocity of expulsion of the particles being low. The possibility of the reversibility of radioactive processes is considered, and regarded as probable in certain cases. Difficulties in connexion with the views expressed are considered. The hypothesis is used to explain the laws (so-called) of the atomic weights of elements of small atomic weight, and the shape of the curve obtained when the atomic weights are plotted against Moseley's numbers. J. F. S.

Dimensions of Atoms. A. O. RANKINE (*Phil. Mag.*, 1920, [vi], **40**, 516—519).—A theoretical paper in which the atomic diameter of argon, neon, krypton, xenon, chlorine, bromine, iodine, oxygen, and nitrogen, as found by Bragg from crystal measurements (this vol., ii, 537), are compared with the values found by the author from viscosity measurements (A., 1910, ii, 188, 409, 829; 1912, ii, 332). It is shown that the values obtained by the latter method are somewhat larger than those obtained by the former, but that the increment in the diameter, in passing from one member of a group to the next, is generally about the same in the two sets of values. J. F. S.

Constitution and Structure of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 157—159).—A continuation of a former paper (this vol., ii, 26), in which elements heavier than manganese are included. The sodium atom is supposed to enter into the constitution of heavier atoms, and the addition of a mass of 23 always corresponds with the gain or loss of one electron. It is shown by calculation that the results cannot be due to chance. J. R. P.

Five Main Principles in the Constitution and Structure of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 182—185).—(1) Single chemical valencies emanate from elements or portions of elements the masses of which are 1, 3, 7, 23, and 39. (2) The non-metallic nature of an element is always due to a pair or pairs of electropositive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unit. (3) Monadic Na (23) takes a prominent part in the formation of all elements of greater mass than itself. (4) In the simpler elements, H (1) forms the connecting link between the other portions, 3, 7, 23, and 39. In the formation of the heavier elements, masses of 23 sometimes unite by forces which are not chemically evident without any intervening unit mass. (5) Each of the heavier elements is formed by the union of simpler elements (which are indicated in each case by mineralogical and chemical facts combined). J. R. P.

Representation of the Periodic System of the Elements by a Three-dimensional Spiral. GEORG SCHALTENBRAND (*Zeitsch. anorg. Chem.*, 1920, **112**, 221—224).—The elements are arranged in order of atomic weight on an eccentric spiral. The spiral has turns of four kinds of increasing circumference. The first, smallest turn carries the elements hydrogen and helium, and is followed by a larger turn corresponding with the first short period of the periodic table. The short turn is then repeated, carrying neon and fluorine, and in successive similar short turns appear an inactive element and a halogen. The long periods of the table are represented by correspondingly large turns of the spiral, and the largest turn of all carries the rare earth elements. Elements belonging to the same group in the periodic table lie in a vertical plane passing through the axis of the spiral. E. H. R.

The Melting Point, Atomic Volume, and the Atomic Number of the Elements, and the Restoring Force of the Atoms. SUMINOSUKE ONO (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 251—260).—By means of Lindemann's formula, approximate but simple quantitative relations between the atomic numbers and melting points, etc., are deduced, and are given in the form of charts. CHEMICAL ABSTRACTS.

Atomic Forces. W. KOSSEL (*Zeitsch. Physik*, 1920, **1**, 395—415. Compare A., 1916, ii, 243).—A discussion of the general nature of chemical bonding. The two main classes are: (1) heteropolar, where the forces are electrostatic and between different kinds of atoms, depending on the valence electrons, and (2) homopolar, generally between the same kind of atoms or molecules. In (2) the bonding is generally due to the holding of outer electrons in common, and their periodic properties can be predicted by assuming that atoms tend to take up electrons to form the stable 8-configurations of the noble gases. The bonds considered may be those between atoms or between molecules, the two being sometimes indistinguishable, as in the case of the sodium chloride lattice. The two classes may be combined, as in the case of silicon tetrachloride, where the submolecular forces belong to (1) and the intermolecular to (2). The haloids of (1) (alkali and alkaline earth) are characterised by decrease of stability (m. p.) with increasing molecular weight of the halogen, whilst those of (2) show the reverse. Many other periodic characteristics are discussed.

CHEMICAL ABSTRACTS.

Percentage Curves of Carbon Compounds. ALEXANDER JANKE (*Oesterr. Chem. Zeit.*, 1920, **23**, 98—101, 106—108).—A mathematical paper in which the numbers of carbon atoms in organic compounds are represented as abscissæ and the percentage of carbon as ordinates. The resulting curve is called a percentage curve. For all hydrocarbons except C_nH_{2n}, these curves are parabolas. For hydrocarbons, C_nH_{2n}, they are straight lines. The [illegible]ence of substitution is considered. J. R. P.

The Theory of Molecular Compounds. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1920, **112**, 81—96).—In certain respects, Werner's co-ordination formulæ, as applied, for example, to the cobaltammines, are unsatisfactory. It is difficult to understand, for instance, in the hexammine chloride, $Co[(NH_3)_6]Cl_3$, how the field of affinity between the cobalt and chlorine atoms can extend over the field of affinity of the ammonia molecules, especially in view of the strong affinity between hydrogen and chlorine. The variation of the total valency of cobalt between 6 and 9 in the cobaltammine group is also difficult to understand. The author applies the principle of "affinity adjustment of the valencies" to overcome the difficulties. In molecular compounds, such as the cobaltammines, the cobalt atom is assumed to have a fixed co-ordinative valence of 6, corresponding with the number of groups in the inner sphere of Werner's formulæ. The ionisable radicles or atoms in the outer sphere are then considered to be combined with the complex radicle as a whole, not attached definitely to the cobalt atom or to any of its associated molecules. The same idea is applied to the complex platinum salts.

Complex organic molecular compounds, such as those formed between aromatic hydrocarbons and di- or tri-nitrobenzene, or between hydrocarbons and quinones, are also considered. There

is, in general, no connexion, for example, between the number of nitro-groups in a compound and the number of aromatic nuclei with which it will combine. In such cases, the compounds are formed by the saturation of polyatomic valence fields on both sides. In some cases it is conceivable that a polyatomic valence field may be saturated by combination with a monatomic field, for instance, when a quinone, with two unsaturated carbonyl oxygen atoms, combines with two benzenoid nuclei. In other classes of compounds, for instance, the compounds between tin tetrachloride and two molecules of a ketone, a compound of the co-ordinative type may be formed, the tin in this case having a co-ordinative valency of 6, thus:

$$\underset{\mathrm{VI}}{SnCl_4}\begin{matrix}\cdot O{:}CR_2\\ \cdot O{:}CR_2\end{matrix}.$$

In the crystal structure of simple organic molecular compounds of the type *AB*, it is probable that each constituent acts as a co-ordination centre, so that complexes of the type AB_6 and BA_6 interpenetrate, as they do in a rock-salt crystal. This would explain the predominance of the simplest type of such molecular compounds. E. H. R.

Back-pressure Valves for Water Filter Pumps. E. Pinoff (*Chem. Zeit.*, 1920, **44**, 671).—To prevent water passing into a flask under exhaustion from a water-pump, owing to an alteration in the water pressure, a simple valve is inserted by means of rubber tubing between the pump and the flask, manometer, etc. This consists of a short glass tube constricted at each end to a small opening. Within this is a short glass rod, one end of which is fitted into a piece of pressure rubber tubing, whilst the other end is somewhat flattened, and also capped with rubber, a narrow space for the passage of air being left between the rubber tubing and the inner wall of the glass tube. The rod is thus movable, and so long as the pump is working normally is forced against the constriction nearest the pump, still leaving a passage for the air, but should any water enter the tube from the pump, the rod is immediately driven back against the other constriction, the opening in which it seals, so that neither water nor air can enter the flask. C. A. M.

Laboratory Apparatus for Delivering Small Quantities of Gas for Admixture with Other Gases in Constant Proportion. Robert Mezger (*Chem. Zeit.*, 1920, **44**, 658—659).—For the delivery of a constant supply of a gas (for example, ammonia) in definite proportion to another gas, the ammonia is generated by heating ammonium chloride and moistened lime in a round-bottomed flask supported in a basin of mercury. Through the stopper of the flask passes one arm of a T-tube, whilst another branch of this is connected with a mercury thermo-regulator controlling the supply of gas to a Bunsen burner beneath the basin. There is also a pilot flame, with an independent gas supply, adjoin-

ing the Bunsen tube. The other outer limb of the T-piece conducts the ammonia into a capillary tube, which is connected with a wider tube, bending first laterally and then upwards to join a second T-piece. One arm of this communicates with a measured supply of a gas or of air, whilst the other is fitted into a reaction tube packed with glass wool. The pressure is shown on a mercury manometer between the ammonia flask and capillary tube. After removal of air from the apparatus by means of ammonia, the flask is connected with the capillary, and the tap communicating with the thermo-regulator opened. As soon as the pressure rises sufficiently, the gas is cut off from the Bunsen burner, and only the minute flame is left, until the pressure falls again, the gas is re-lighted from the pilot flame, and ammonia again evolved, and so on continuously. The regulation of the ammonia supply is effected by means of the capillary tube. For a definite capillary and kind of gas, the consumption of the gas (in this case ammonia) in c.c. per second (v) is found by means of the following modification of Poiseuille's formula, $v=K.H$, where H represents the difference of pressure and K a constant depending on the capillary and the gas used. In the case of ammonia, it may be found by varying the difference in pressure and estimating each time the corresponding amounts of ammonia by absorption in standard sulphuric acid. By plotting the results for v in a co-ordinate system, the volume of gas corresponding with any required pressure may be read directly. C. A. M.

Lecture Demonstration of the Instantaneous Combination of Bromine with Hydrogen and of the Chlorination of Magnesium in the Form of Magnesium Wool. OTTO OHMANN (*Ber.*, 1920, **53**, [*B*], 1429—1430).—Bromine (four to six drops) is placed in a litre gas cylinder, which is shaken until complete evaporation has occurred. The cylinder is brought mouth to mouth with a similar jar filled with hydrogen, and, when diffusion has taken place, the mixture is ignited with a red-hot wire. Combination occurs instantaneously with a perfectly harmless explosion, which is due to the union of excess of hydrogen with residual atmospheric oxygen. If more bromine is used, and, in consequence, less air is left, union occurs at once and without explosion, but with production of a peculiar blue flame.

A pad of magnesium wool, lightly sprinkled with finely divided antimony, is fixed to an iron wire and plunged into a jar of chlorine. The spontaneous ignition of the antimony causes the magnesium to burst into vigorous combustion, yielding a product which covers the whole of the inside of the vessel in the form of a snow-white, voluminous powder. H. W.

Lecture Experiments. Critical Examination of well-known Experiments with Metallic Sulphides. R. WINDERLICH (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 100—103; from *Chem. Zentr.*, 1920, iii, 429).—Strictly speaking, the union of iron and sulphur cannot be used as an illustration of the

law of constant composition or as an obvious illustration of the differences between mixtures and compounds. A mixture is preferably demonstrated by finely powdered quartz and salt; the mixture of flowers of sulphur and iron filings affords a simple example of a chemical process which, started at one point, proceeds through the whole mass by reason of the great heat of reaction. The statement, common in many elementary text-books, that hydrogen sulphide does not give a precipitate with solutions of ferrous salts is only true when the latter contain mineral acid. The proportions of sulphur and oxide of iron prescribed for demonstration are not in accordance with the amounts calculated from the equation $2Fe_2O_3 + 7S \longrightarrow 4FeS + 3SO_2$, partly because an excess of sulphur must be taken to counterbalance that lost by volatilisation, and partly to inhibit the formation of sulphate, which occurs in the presence of a deficiency of sulphur.

H. W.

Inorganic Chemistry.

The Preparation of Chlorine from Hydrochloric Acid or Chlorides by means of Nitric Acid. JULIUS BAUMANN (*Chem. Zeit.*, 1920, **44**, 677).—The chlorine in chlorides or hydrochloric acid can be converted quantitatively into free chlorine by the action of nitric acid of about 52·0% strength, and the whole of the nitric acid recovered unchanged when the proper working conditions are observed. The points to be observed are to charge the chloride, for example, sodium chloride, slowly into the boiling acid and to use a long dephlegmator, whilst a current of air passes into the reacting gases. The following gas reactions involved, namely, $NOCl + HNO_3 = N_2O_4 + HCl$, $2HCl + N_2O_4 = N_2O_3 + Cl_2 + H_2O$, and $N_2O_3 + O_2 + H_2O = 2HNO_3$, then have time to complete themselves, and chlorine passes over practically free from hydrochloric acid, whilst the whole of the nitric acid flows back into the reaction vessel.

E. H. R.

Electrolytic Formation of Perchlorate from Chlorate. J. GUILFOYLE WILLIAMS (*Trans. Faraday Soc.*, 1920, **15**, 134—137). —The production of perchlorate by electrolysis is considerably improved if a higher temperature of the liquid is maintained, and the frequent addition of acid improves the efficiency still more. During electrolysis, chloride is produced, and there is an equilibrium value for each temperature.

J. R. P.

The Relationship of Iodine and Bromine to Oxygen. G. GRUBER (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 107—108; from *Chem. Zentr.*, 1920, iii, 434).—Direct replacement of bromine by iodine occurs when the latter acts on an aqueous solution of

potassium bromate; a similar action is not observed with bromine and potassium chlorate. Iodine attacks potassium chlorate in a ·ss simple manner than potassium bromate, the change passing rough the phases indicated by the equations $2KClO_3 + 2I + H_2O = HI_2O_6 + KCl + HClO$, $KHI_2O_6 + KCl + HClO = 2KIO_3 + H_2O + Cl_2$, ıd $3HClO = HClO_3 + 2HCl$. H. W.

Preparation of Thionyl Fluoride and Attempts to Prepare arbonyl Fluoride. WILHELM STEINKOPF and JULIUS HEROLD *I. pr. Chem.*, 1920, [ii], **101**, 79—81).—A modified method of reparing thionyl fluoride by the interaction of thionyl chloride nd arsenic fluoride is described. A brass flask is provided with n upright condenser, which is connected by a bent tube to a second ondenser cooled with ice-water, which leads to a leaden vessel ooled to −50° to −60°. The flask is initially cooled by ice and ontains the arsenic fluoride, to which the calculated quantity of hionyl chloride is gradually added through a dropping funnel; he latter is then removed, and the flask is slowly warmed to about 0°, when the thionyl fluoride distils into the leaden receiver, whilst rsenic fluoride and chloride and thionyl chloride are held back by he reflux condenser. The attempts to prepare carbonyl fluoride vere not completely successful, probably because platinum pparatus was not available. The best results were obtained by eating a mixture of arsenic fluoride and carbonyl chloride in a ead-lined iron or brass vessel provided with an upright condenser; he process is carried out during several hours on the water-bath vith intermittent condensation of the products. Impure *carbonyl luoride* was thus obtained as a readily decomposable substance, which solidified in liquid air and had b. p. about −160° to −150°. H. W.

The Decomposition of Persulphuric Acid. HERMAN PALME *Zeitsch. anorg. Chem.*, 1920, **112**, 97—130).—The rate of decomosition of potassium persulphate in solutions of 5·0, 7·53, and 0N-sulphuric acid at 50° has been studied. Since the reaction roceeds through the stages, persulphuric acid ⟶ Caro's acid ⟶ ıydrogen peroxide, it was necessary to develop a method for stimating these substances when all present in the same solution. Advantage was taken of the fact that Caro's acid reacts immediıtely with potassium iodide, whilst hydrogen peroxide reacts much nore slowly, and persulphuric acid slowest of all. A sample of he solution is mixed with potassium iodide and titrated rapidly vith sodium thiosulphate, the time taken being noted, so that a orrection can be applied for the small quantity of iodine liberated y the hydrogen peroxide and persulphuric acid. The quantity f Caro's acid is thus found. A second sample is then treated with otassium iodide and titrated with sodium sulphite, which reduces ıydrogen peroxide. This second titration gives the sum of Caro's ıcid and hydrogen peroxide. Finally, the persulphuric acid is stimated in a third sample by adding the calculated quantity of

sodium sulphite to reduce the other two compounds, and estimating the persulphuric acid by the ferrous sulphate–permanganate method. The dilution for the titrations corresponded with 2·0 grams of potassium persulphate per litre, of which 200 c.c. were titrated at a time.

The experiments showed that, within the limits of error, the two reactions, $H_2S_2O_8 + H_2O \overset{k_1}{=} H_2SO_5 + H_2SO_4$ and $H_2SO_5 + H_2O \overset{k_2}{=} H_2O_2 + H_2SO_4$, can be regarded as unimolecular and irreversible. With increasing concentration of sulphuric acid, both velocity-constants increased at a greater rate than the acid concentration, but the ratio k_1/k_2 remained constant, 39·8. No relation between hydrogen-ion concentration and velocity of reaction could be discovered, and the conclusion of Levi and Migliorini (A., 1907, ii, 81) that undissociated persulphuric acid, the presence of which would be favoured by increasing hydrogen-ion concentration, is less stable than its salts, was not confirmed. The experiments were not carried far beyond the time after which oxygen begins to be evolved, through the reaction $H_2S_2O_8 + H_2O_2 = 2H_2SO_4 + O_2$, but it was shown that the velocity of this reaction increases considerably with decreasing concentration of acid. Friend's results (T., 1906, **89**, 1092), which showed that the reaction is unimolecular, can be explained on the assumption that Caro's acid is first formed from persulphuric acid, and then reacts with hydrogen peroxide. Persulphuric acid probably does not itself react with hydrogen peroxide. E. H. R.

Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. III. W. E. Adeney and H. G. Becker (*Sci. Proc. Roy. Dublin Soc.*, 1920, **16** [N.S.], 143—152).—A continuation of experiments previously reported (see A., 1919, ii, 104, 510). The rate of solution of air in quiescent water under laboratory conditions was determined. The results show that the process of solution under these conditions consists in solution at the surface with slow mixing in the body of the liquid. The results are represented by a formula, $dw/dt = a - bw$, where w = total quantity of gas in solution at any moment, t = time, and a and b are constants depending on the size of the apparatus. The water was contained in vertical tubes exposed to air. The rate of solution depends on the humidity of the air, being greater with dry than with moist air. J. R. P.

Very High Pressures and the Synthesis of Ammonia. Georges Claude (*Bull. Soc. chim.*, 1920, [iv], **27**, 705—724).—A lecture delivered before the French Chemical Society and the Society for the Encouragement of National Industry. W. G.

Fractionation of Nitric Acid. Julius Baumann (*Chem. Zeit.*, 1920, **44**, 678).—Experiments on the fractionation of nitric acid were made, using a litre flask fitted with a dephlegmator 200 cm. long, inclined at 45°, with a jacket for heating it to any desired temperature. A mixture of 250 c.c. of water and 250 c.c. of

nitric acid (D 1·4; 69·8%, the constant boiling mixture) was distilled with the dephlegmator heated at 100°, and there were obtained 250 c.c. of distillate, containing only 0·02% HNO_3, and 250 c.c. of residual nitric acid, 69·5% in strength. Practically complete separation was therefore obtained. In another experiment, 500 c.c. of 91·5% HNO_3 were distilled with the dephlegmator heated at 86°, the boiling point of pure nitric acid. There were obtained in the distillation flask 140 c.c. of 70·1% HNO_3, and in the receiver 350 c.c. of 100·5% HNO_3. Thus a practically complete separation into pure nitric acid and the constant boiling mixture, b. p. 123°, was obtained. E. H. R.

Reduction of Nitrites and Nitrates. OSCAR BAUDISCH and PAUL MAYER (*Biochem. Zeitsch.*, 1920, **107**, 1—42).—Nitrites are reduced quantitatively by excess of ferrous hydroxide in neutral and alkaline solution. In boiling solutions made alkaline with carbonates, nitrous oxide and ammonia are chiefly formed. In boiling alkali hydroxide solution, the nitrite is quantitatively reduced to ammonia. Alkali nitrates are reduced quantitatively by ferrous hydroxide in neutral solution and in alkaline solution containing 28% of sodium hydroxide. Starting with neutrality, the amount of nitrate reduced diminishes until the alkali content is 6·5% of sodium hydroxide, when a minimum is reached; beyond that limit, the amount reduced increases with the increase of alkali until the maximum is reached at the concentration of 28% of sodium hydroxide. Up to a concentration of 6·5% of sodium hydroxide, oxygen is necessary for the reduction. With higher alkali concentrations, reduction also takes place in the absence of oxygen. At an alkali concentration of 6·5% of sodium hydroxide, the amount of nitrate reduced is proportional to the amount of nitrate present in solution, and is in a condition of adsorption by the ferrous hydroxide. The above observations are utilised for the estimation of nitrites and nitrates separately and when together. S. S. Z.

Equilibrium of the Four-component System: Na_2SO_4, $NaHCO_3$, $(NH_4)_2SO_4$, NH^4HCO_3 and H_2O. KYOSUKE NISHIZAWA (*J. Chem. Ind. Tokyo*, 1920, **23**, 25—43).—To study the best condition for the manufacture of ammonium sulphate by the ammonia–soda process from sodium sulphate, detailed studies were made of the equilibrium of a system consisting of these four components, first 2-component, then 3-component, and finally 4-component systems being determined. Ammonium hydrogen carbonate was prepared for each experiment. The concentration of the sodium sulphate and the ammonium sulphate was determined by the barium chloride and the Kjeldahl methods, respectively, and that of both bicarbonates by titration, using methyl-orange as indicator. The results are tabulated in sixteen tables and two curves. The results obtained from invariant systems are as follows:

Solid Phases.	Composition of the solution in gram-mol. to 1000 gram-mol. H_2O. Na_2SO_4.	$(NH_4)_2SO_4$.	NH_4HCO_3.	$NaHCO_3$.
$Na_2SO_4,10H_2O$	16·61	—	—	—
$(NH_4)_2SO_4$	—	10·05	—	—
NH_4HCO_3	—	—	42·52	—
$NaHCO_3$	—	—	—	18·53
$Na_2SO_4,10H_2O$; $NaHCO_3$.	14·18	-	—	12·75
$Na_2SO_4,10H_2O$; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	31·54	45·14	—	—
$Na_2SO_4,(NH_4)_2SO_4,4H_2O$; $(NH_4)_2SO_4$	13·74	94·86	—	—
$(NH_4)_2SO_4$; NH_4HCO_3	—	96·40	14·91	—
$NaHCO_3$; NH_4HCO_3	—	—	38·92	12·79
$Na_2SO_4,10H_2O$; $NaHCO_3$; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	26·22	45·86	—	12·84
$NaHCO_3$; NH_4HCO_3 ; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	12·46	67·08	—	20·90
NH_4HCO_3 ; $(NH_4)_2SO_4$; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	6·79	97·99	—	14·96

CHEMICAL ABSTRACTS.

Cæsium Bromate. C. R. McCrosky and Harold D. Buell (*J. Amer. Chem. Soc.*, 1920, **42**, 1786—1789).—The preparation of cæsium bromate is probably best carried out in acid solution. Cæsium bromate is a definite crystalline salt without water of crystallisation. Occluded water causes decrepitation. Its melting point (not yet determined) is above that of potassium bromate. After fusion, the salt soon decomposes, evolving a large amount of oxygen and leaving a bromide. The solubility of the salt is 4·53 grams in 100 grams of water at 30°. J. R. P.

* **A New Rubidium (Cæsium)-Silver-Gold Compound and its Application to the Microchemical Detection of Gold, Silver, Rubidium, and Cæsium.** Erich Bayer (*Monatsh.*, 1920, **41**, 223—241. Compare Emich, A., 1919, ii, 171).—Characteristic crystalline precipitates are formed when solutions of rubidium or cæsium chloride are mixed with gold and silver solutions; rubidium-silver-gold chloride forms blood-red prisms and platelets, whilst the cæsium compound crystallises in opaque cubes and stars. The composition of the compounds corresponds with the formulæ $Ag_xAu_{2-x/3}Cl_6,3RbCl$ and $Ag_xAu_{2-x/3},Cl_6,3CsCl$ (where $0 \leq x \leq 6$), in which gold and silver are mutually replaceable components. For rubidium, silver, and gold, the atomic proportions observed are in the ratio 3:0·81—1·04:1·5—1·4, whilst for the cæsium compound the corresponding ratio is 3:0·4—1·18:1·82—1·64. The limiting compounds, Ag_2CsCl_3 and $Au_2Cs_3Cl_9$, do not appear to have been prepared, but Marsh and Rhymes (T., 1913, **103**, 782) have examined the analogous substances, Ag_2CsI_3 and Ag_2RbI_3.

The crystals are adapted to the microchemical identification of gold, silver, rubidium, and cæsium, the smallest quantities recognisable in this manner being 0·1, 0·01, 0·1, and 0·1 microgram respectively. H. W.

A New Rubidium (Cæsium)-Silver-Gold Compound and its Application to the Microchemical Detection of Gold, Silver, Rubidium and Cæsium. FRIEDRICH EMICH (*Monatsh.*, 1920, **41**, 243—252. Compare Bayer, preceding abstract; Emich, A., 1919, ii, 171).—A theoretical paper in which ideas are developed based on Bayer's observation that univalent silver and tervalent gold are mutually replaceable in the rubidium (cæsium)-silver-gold chlorides.

It is suggested that elements in general have a far greater power of mutual replaceability than has previously been assumed, and that this is frequently the cause of the great difficulty experienced in isolating absolutely pure substances. Elements in general may be classified as (1) isotopic elements, the separation of which is impossible by precipitation or crystallisation; (2) isomorphous elements, which can only be incompletely separated; and (3) readily separable elements. The most general conception of the union of two substances is obtained by regarding it as controlled by the two factors, affinity in the narrower sense, due to the attraction of the atoms or molecules caused by harmonic vibration, and cohesive forces in the sense of the entropy rule. Both influences are, in general, operative, but the first predominates in chemical compounds, the second in isomorphous and isotopic mixtures. Between the limiting cases, which are generally well defined, because the controlling factors are usually of a widely differing order of magnitude, there are a number of transition examples, such as the rubidium-gold-silver compounds. It should be noted that this hypothesis involves the consideration of the laws of constant and multiple proportions, like the gas laws, as only approximately accurate.

Bayer's compounds are discussed at length, and it is pointed out that the limiting compounds, $RbCl,2AgCl$ and $3RbCl,2AuCl_3$, are not known, and that the stability of the molecule is increased by the entrance of a third component, and that the heavier cæsium has a more marked effect than the lighter rubidium. Re-examination of the triple nitrites has proved that there is a greater tendency towards mutual replacement among the bivalent than among the univalent elements, but the phenomena are not so well defined as with Bayer's salts.

Contrary to the previous observation (Emich, *loc. cit.*), it is now found that the place of rubidium cannot be taken by potassium in the triple chloride, and the value of the method for the microchemical detection of cæsium and rubidium is thereby greatly enhanced. H. W.

Ammonium Silicate. IV. The Ageing and Transformation of Silicic Acid Gel and the Course of the Solution of Silicic Acid in Ammonia. ROBERT SCHWARZ and OTTO LIEDE (*Ber.*, 1920, **53**, [*B*], 1509—1518. Compare this vol., ii, 175; A., 1917, ii, 31; 1919, ii, 283).—The authors have examined the behaviour of silica gel when slowly dried at the ordinary temperature and are led to the conclusion that the age-

ing process consists in the condensation of $(SiO_2)_x$ to $(SiO_2)_{2x}$, and that this occurs without any change in the appearance of the gel; further changes in the system SiO_2–H_2O then occur, leading to the formation of $(SiO_2)_{3x}$, which is indicated by the incipient formation of cloudy particles in the colourless, transparent mass. Precisely similar phenomena are observed when the gel is dehydrated by being heated, but, for some unexplained reasons, a much greater loss of water appears to be necessary in this case before the end-point is reached.

The solubility of silicic acid in ammonia has been examined in a modified manner, since it has been found that the older measurements, in which glass vessels were used, are very greatly influenced by the alkali from the glass. The hydrated silica and ammonia are mixed in the quartz vessel which serves for the measurement of the electrical conductivity. After definite intervals, portions of the solution are filtered through paper, which retains suspended silica, and the filtrates are passed through an ultra-filter to retain colloidal particles. The silica retained by the paper and that in the final filtrate are estimated. It is found that equilibrium is attained after about seventy-two hours at 18°, and that the solution contains 64% of the silica in true solution, 8% in colloidal solution, and 28% undissolved. The conductivity and solubility curves show that the amount of dissolved silica increases during the whole course of the experiment, whilst the colloidal silica gradually diminishes in quantity. The former therefore grows at the expense of the latter, and it appears justifiable to conclude that the formation of the colloidal solution is the primary process which is followed by the production of the molecular solution.

H. W.

Solubility of Calcium Carbonate. YUKICHI OSAKA (*J. Tokyo Chem. Soc.*, 1920, **41**, 453—468).—On the assumption that only a small part of the carbon dioxide dissolved in water is combined with the water, and that consequently carbonic acid is a much stronger acid than acetic acid, the author has recalculated the solubility product of calcium carbonate from the data of McCoy and Smith on the solubility of calcium carbonate under different carbon dioxide pressures, using $K=3\cdot50\times10^{-7}$, $K_2=4\cdot91\times10^{-11}$, and has obtained the value $7\cdot24\times10^{-9}$. The number of gram-molecules of calcium carbonate dissolved by 1 litre of water (C) under any known carbon dioxide pressure (P) is given by the formula

$$C=[Ca^{\cdot\cdot}]+(1-y)/2y[HCO_3{}']\text{,}$$

where $Ca^{\cdot\cdot}=(5\cdot24\times10^{-17}+2\cdot49\times10^{-12}P^{\frac{2}{3}}+2\cdot97\times10^{-8}P^{\frac{4}{3}})/(2\cdot91\times10^{-6}P)$ and $HCO_3{}'=(2\cdot61\times10^{-6}P)/(7\cdot24\times10^{-9}+1\cdot72\times10^{-4}P^{\frac{2}{3}})$, and y = the degree of dissociation of calcium acetate having the same concentration of acetate ion as the bicarbonate ion.

CHEMICAL ABSTRACTS.

Monoclinic Double Selenates of the Copper Group. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 67—95).—The

four double selenates of the series $R_2M(SeO_4)_2,6H_2O$, in which M is copper and R is potassium, rubidium, cæsium, or ammonium, have been examined crystallographically. They form a group in the extensive series of isomorphous monoclinic double sulphates and selenates which have been examined by the author, and the four salts exhibit the same relationships one to another as in similar groups of potassium, rubidium, cæsium, and ammonium salts. As was found in the case of the double sulphates, so in the double selenates, the constants, both physical and morphological, of the salts of the copper group differ considerably in their absolute values from those of the magnesium, zinc, iron, nickel, and cobalt groups (A., 1919, ii, 346).

The salts all crystallise in the holohedral-prismatic class of the monoclinic system. Potassium copper selenate, $K_2Cu(SeO_4)_2,6H_2O$, $a:b:c=0.7508:1:0.5143$, $\beta=103°25'$, D_4^{20} 2·539. Rubidium copper selenate, $Rb_2Cu(SeO_4)_2,6H_2O$, $a:b:c=0.7495:1:0.5066$, $\beta=104°44'$, D_4^{20} 2·839. Cæsium copper selenate,

$Cs_2Cu(SeO_4)_2,6H_2O$,

$a:b:c=0.7398:1:0.4981$, $\beta=105°42'$, D_4^{20} 3·073. Ammonium copper selenate, $(NH_4)_2Cu(SeO_4)_2,6H_2O$, $a:b:c=0.7476:1:0.5150$, $\beta=105°30'$, D_4^{20} 2·223.

The optical constants of the crystals were determined, and for each salt the axial ratios of the optical indicatrix and the molecular refraction and dispersion were calculated. E. H. R.

Comparative Study of the Decomposition of a Dissociable Mercurous Chloride obtained from Mercuric Chloride and of the Ordinary Form. GAMBIER (*Ann. malad. vénér.*, **15**, 28—31; from *Chem. Zentr.*, 1920, iii, 331).—Duret's observations (A., 1919, ii, 232) are confirmed, and, by variation of the precipitating and reducing agent, it has been found possible to secure a more voluminous and still more readily dissociable preparation which is quite free from mercuric chloride. The separation of free mercury has been estimated colorimetrically. The preparation gives 2·0 times at 15°, 2·4 times at 30°, 2·66 times at 60°, and 1·5 times at 100° as much mercury as does ordinary calomel, and the equilibrium between eliminated mercury and the unchanged molecule is very rapidly attained. H. W.

Inflammation of a Mixture of Aluminium and Sodium Peroxide by means of Water. OTTO OHMANN (*Ber.*, 1920, **53**, [*B*], 1427—1429).—An intimate mixture of finely divided aluminium (1 gram) and sodium peroxide (4·3 grams) is readily inflamed with slight explosion by the addition of a few drops of water. The experiment is best adapted to lecture purposes by sprinkling a small quantity of the powder on the surface of water, when it forms a thin skin without becoming inflamed; subsequent addition of more powder is then accompanied by inflammation. The suitability of the specimen of sodium peroxide should be ascertained, as its quality is liable to considerable variation.

H. W.

The Oxidising Properties of Sulphur Dioxide. I. Iron Chlorides. WILLIAM WARDLAW, and FRANCIS HERBERT CLEWS (T., 1920, **117**, 1093—1103).

The Oxidising Properties of Sulphur Dioxide. II. Iron Phosphates. WILLIAM WARDLAW, SIDNEY RAYMOND CARTER, and FRANCIS HERBERT CLEWS (T., 1920, **117**, 1241—1247).

Oxydase-like Action of Some Complex Salts of Metals. YUJI SHIBATA and KEITA SHIBATA (*J. Tokyo Chem. Soc.*, 1920, **41**, 35—53. Compare Colin and Liévin, A., 1919, i, 430).—Using a 0·001*M*-alcoholic solution of myricetin to indicate the oxydase-like action, the authors have examined about fifty complex salts of cobalt, nickel, copper, zinc, cadmium, chromium, and iron, and find that the most reactive salts are those containing strong acid radicles or metals which give unstable complex ions in aqueous solution; for example, 1:6-dichlorotetramminecobalt chloride (in 0·001*M* solution) produces a bright red or purple coloration instantly, pentamminecupric sulphate less markedly, dichloroethylenediaminechromium chloride very feebly, and potassium ferro- or ferricyanide not at all.

The four factors which operate against the oxydase-like action are (1) hydrogen ions, (2) inactive complex salts, (3) hydroxylamine, mercuric chloride, and a few other substances, (4) heating at 80—90°. Valency plays no part, the reaction depending wholly on the instability of the salts in water.

The application of these active complex salts to lacquers hastens drying to a marked degree. CHEMICAL ABSTRACTS.

Salts of Stannic and Plumbic Acids. HANS ZOCHER (*Zeitsch. anorg. Chem.*, 1920, **112**, 1—66).—A study of stannates and plumbates was undertaken with the object of elucidating the so-called semi-colloidal state, with a critical discussion of which the paper opens. The methods for preparing and analysing alkali stannates are described. Sodium stannate crystallises from sodium hydroxide solutions at ordinary temperatures as the trihydrate, $Na_2Sn(OH)_6$; it is practically insoluble in 7·0*N*-sodium hydroxide. When precipitated by sodium hydroxide at 0° or by alcohol at 0° or ordinary temperatures, it forms the tetrahydrate,

$$Na_2Sn(OH)_6,H_2O.$$

The solubilities of the two hydrates were determined between -5° and 50°; that of the trihydrate, the less soluble salt, which may be regarded as an "anhydride," diminishes with increasing temperature, whilst that of the tetrahydrate increases. The transition point was difficult to determine by the dilatometric method, but from the solubility curves appears to be close to −5°. The trihydrate forms a eutectic with water at −11°, the tetrahydrate at −7°. In addition, a third hydrate, approximating to $Na_2Sn(OH)_6,18H_2O$, was discovered, which has a transition point to the "anhydride" at 1°. The hydrolysis of sodium stannate in aqueous solutions was

studied by means of potential measurements. In normal solutions the hydrolysis is about 2·7%, and appears to be complete at a dilution of $1/3000N$. In normal solutions of the stannate the extent of hydrolysis gradually increases with time. This phenomenon is discussed in connexion with similar observations in the case of other colloidal solutions and of solutions of tin tetrachloride. There is no evidence of adsorption of alkali by sodium stannate under any conditions.

Lithium stannate forms an "anhydride," $Li_2Sn(OH)_6$, isomorphous with the sodium salt, and also a dihydrate of this salt, $Li_2Sn(OH)_6,2H_2O$ The solubilities of both salts were determined between 28° and 80°. The two curves are approximately parallel, the solubilities increasing with the temperature; the transition point could not be found, but is probably below 100°. Potassium stannate forms an "anhydride," $K_2Sn(OH)_6$, and also a mono- and di-hydrate of this salt. The solubilities are greater than those of the sodium and lithium salts.

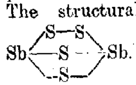
In the course of a long discussion on the chemistry of stannic oxide from the colloidal point of view, the following points are elucidated. The low crystallisation velocity of the oxide, resulting from its slight solubility, facilitates its assumption of the colloidal state. The "ageing" of the colloid is accelerated or retarded by various influences, particularly by accompanying salts in solution. Coagulation, that is, the coalescence of the bounding surfaces of the colloidal particles in solution, is retarded by the electrostatic charge on the particles.

The work was also extended to the plumbates. Sodium plumbate was prepared by dissolving freshly precipitated lead peroxide, in small quantities at a time, in boiling concentrated (8—10N) sodium hydroxide solution. The salt is very sparingly soluble in this solution, and separates in crystals which appear to be isomorphous with sodium stannate. Although the analyses of the crystals always showed excess of Na_2O, their composition is taken to be $Na_2Pb(OH)_6$. Lithium plumbate was also prepared, and appeared, from its crystalline form, to be isomorphous with the sodium salt. The properties of plumbic acid are discussed from the colloidal point of view. E. H. R.

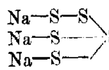
Antimony Pentasulphide (Sulphur auratum). F. KIRCHHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 67—80).—The ordinary golden antimony sulphide is described in the literature as consisting of a mixture of pentasulphide and trisulphide, with more or less free sulphur. The purest form of the substance contains about 8% of sulphur, which can be extracted with carbon disulphide or acetone, the residue having a composition corresponding with the formula Sb_2S_4. This form is obtained by the action of dilute acids on Schlippe's salt, according to the equation $2Na_3SbS_4 + 6HCl \longrightarrow Sb_2S_4 + S + 6NaCl + 3H_2S$. It is shown in the present paper that antimony pentasulphide has no existence, but that golden antimony sulphide is a mixture of Sb_2S_4 with from 0 to 50% Sb_2S_3 and a vary-

ing amount of free sulphur, according to the method of preparation. The compound Sb_2S_4 has been prepared in a pure state from zinc thioantimonate. The latter salt, $Zn_3Sb_2S_8$, was prepared by the interaction of Schlippe's salt and zinc chloride. It formed a chrome-yellow precipitate, which when dried and ground had a bright orange-red colour. The crude substance contained about 6·7% of extractable sulphur, and after removal of this, its composition corresponded exactly with the above formula. The zinc thioantimonate is decomposed by dilute acids according to the equation $Zn_3Sb_2S_8 + 6HCl \longrightarrow Sb_2S_4 + 3ZnCl_2 + H_2S_2 + 2H_2S$. Analysis of the orange-red residue from this reaction showed it to have the composition Sb_2S_4, the same as that of the pure extracted orange form of golden antimony sulphide.

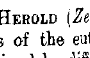
The sulphide Sb_2S_4 is to be regarded as a special case of compounds of the type $M_x(SbS_4)_y$, in which M becomes Sb and $x = y$. The structural formula suggested for the compound is



For the corresponding sodium salt (Schlippe's salt) the structure becomes



and a corresponding formula is suggested for the zinc salt. The colour of the compound Sb_2S_4 and of the thioantimonates of the heavy metals is attributed to the presence of closed ring systems in the structure of these compounds. The sodium salt, in which there is no closed ring, is colourless. The red antimony trisulphide probably has the structure



E. H. R.

Revision of the Atomic Weight of Bismuth. Analysis of Bismuth Chloride. O. Hönigschmid and L. Birckenbach (*Zeitsch. Elektrochem.*, 1920, **26**, 403—408).—See this vol., ii, 549.

The Binary System Lead–Bismuth. W. Herold (*Zeitsch. anorg. Chem.*, 1920, **112**, 131—154).—The limits of the eutectic range in the lead–bismuth alloys have been determined by different observers, generally by thermal methods, with divergent results. These limits have now been investigated by studying the electrical conductivity and hardness of the alloys and their microscopic structure. Special precautions were taken to obtain uniform specimens by careful annealing. The conductivity experiments, which were made at 123° and 0°, indicated for the limit of solubility of bismuth in lead, 17·5 to 18·5% Bi, and for the solubility of lead in bismuth, 1·6% Pb. The interpretation of the results of the hardness experiments was uncertain owing to the influence of the treatment which any particular sample had undergone on its hardness. The hardness–composition curve had a wave-form with an inflexion corresponding approximately with the eutectic point. The hard-

ness of the eutectic does not appear to derive additively from that of the two series of mixed crystals. The curve indicates the mixed crystal limit on the lead side at about 17—18% Bi. The microscopic experiments showed that a sample containing 40% Bi contained no trace of eutectic after annealing eight hours at 124°. Alloys with more than 40% Bi showed eutectic after thirty hours at 40°. It is concluded that the two limits for the eutectic are 40% Bi and 0·2—0·5% Pb. E. H. R.

Normal Bismuth Tungstate and Molybdate: their Relations to the Corresponding Lead Compounds. F. ZAMBONINI (*Gazzetta*, 1920, **50**, ii, 128—146).—The author has prepared and examined, especially crystallographically, normal bismuth tungstate and molybdate, and has subjected the two systems, $PbWO_4-Bi_2(WO_4)_3$ and $PbMoO_4-Bi_2(MoO_4)_3$, to thermal analysis.

Normal bismuth tungstate, $Bi_2(WO_4)_3$, is dimorphous, and crystallises in (1) the monoclinic system, $a:b:c=1\cdot006:1:1\cdot520$, $\beta=90°34'$, $D^{7\cdot5}$ 8·24, and (2) the tetragonal system, $a:a=1:1\cdot566$. The latter phase corresponds perfectly with the tetragonal phase both of the normal molybdates and tungstates of the elements of the yttrium and cerium group, as well as of those of the isomorphogenic elements of the calcium–strontium–barium–lead group, the value of $a:c$ in these compounds varying from $1:1\cdot542$ to $1:1\cdot623$. The monoclinic form is distinctly pseudo-tetragonal, the axial ratios differing but little from $1:1:1\cdot566$ and the value of β but little from 90°. This monoclinic form exhibits undeniable crystallographic resemblances to raspite, the monoclinic form of lead tungstate, but the tetragonal bismuth tungstate shows far closer resemblances to stolzite, the tetragonal form of lead tungstate.

Normal bismuth molybdate, $Bi_2(MoO_4)_3$, was obtained only in the tetragonal form, $a:c=1:1\cdot5636$, D^{15}_{15} 6·07, the crystallographic constants and the molecular volume differing little from those of the molybdates of the cerium metals and of lead.

Monoclinic bismuth tungstate has m. p. 832°, tetragonal bismuth molybdate, m. p. 643°, and lead tungstate and molybdate, m. p. 1130° and 1065° respectively. For the system $Bi_2(WO_4)_3-PbWO_4$ the melting-point diagram has the form characteristic for binary mixtures, either forming no solid solutions or exhibiting extremely limited mutual solubility in the solid state. The crystallisation curve first falls rapidly from 1130° to a eutectic point at about 813° corresponding with about 73 mol. % of $Bi_2(WO_4)_3$, and then rises directly to 832°. The system $PbMoO_4-Bi_2(MoO_4)_3$ shows quite similar behaviour, the crystallisation curve descending rapidly from 1065° to a eutectic at about 615°, corresponding with about 71·5 mol. % of $Bi_2(MoO_4)_3$, and then rises directly to 643°. With both systems the form of the curve of eutectic arrests indicates that the eutectic disappears completely only in the pure components.

T. H. P.

Mineralogical Chemistry.

Zinc-blende in the Basalt of Bühl, near Cassel. W. Eitel (*Centr. Min.*, 1920, 273—285).—Black zinc-blende intimately associated with quartz, and sometimes pyrrhotite or pyrites, occurs as enclosures in the basalt. Analyses show it to be of the marmatite variety with FeS : ZnS = 1 : 4 and 1 : 3 in the two analyses respectively:

	Fe.	Mn.	Zn.	Cd.	S.	Gangue.	Total.	Sp. gr.
I.	12·28	trace	52·02	—	32·08	3·52	99·90	—
II.	19·50	trace	48·08	trace	31·79	0·98	100·35	4·033

The presence of the mineral is attributed to the basalt breaking through a mineral-vein and enveloping fragments of the same. It is supposed that the original pyrites was largely dissociated to ferrous sulphide, which was partly absorbed by the zinc sulphide, the remainder being represented by the pyrrhotite. L. J. S.

Ultrabasite, a New Mineral from Freiberg, Saxony. V. Rosický and J. Štěrba-Böhm (*Zeitsch. Kryst. Min.*, 1920, **55**, 430—439; *Rozpr. České Akad.*, 1916, **25**, No. 45).—The black crystals with metallic lustre and black streak are orthorhombic ($a:b:c = 0·988:1:1·462$) with a tetragonal habit. H 5, D 6·026. They are associated with quartz, rhodochrosite, galena, and proustite on gneiss. Analysis gave:

Sb.	Ag.	Pb.	Cu.	Fe.	Ge.	S.	Total.
4·60	22·35	54·16	0·47	0·25	2·20	16·15	100·18

agreeing with the ultrabasic formula $Sb_4Ag_{22}Pb_{28}Ge_3S_{53}$. The finely powdered mineral is slowly decomposed by digestion with hydrochloric or nitric acid, with separation of some sulphur. It is readily decomposed by fusion with alkali carbonates and nitrate, and the solution gives with the Marsh test a characteristic germanium mirror. Germanium was also detected in cylindrite from Bolivia by this method. A rough separation of germanium and antimony was effected by carefully acidifying with dilute sulphuric acid the solution of the sulphides in sodium sulphide, the bulk of the germanium remaining in solution whilst antimony was precipitated. L. J. S.

Minerals from Tsumeb, S.W. Africa. O. Pufahl (*Centr. Min.*, 1920, 289—296).—Zinciferous tennantite, occurring either alone (anal. I, D 4·61) or intimately associated with galena (II), is massive, with black colour and greenish lustre and a dark cherry-red streak.

	S.	As.	Sb.	Cu.	Zn.	Pb.
I.	23·35	17·94	4·66	43·60	9·24	0·22
II.	22·65	19·65	4·03	43·19	9·27	0·08

	Fe.	Ag.	Au.	SiO_2.	Total.
I.	0·03	0·11	0·01	0·97	100·13
II.	0·17	n.d.	n.d.	0·81	99·85

Mimetite occurs in the secondary zone as compact masses and as almost colourless, prismatic crystals (anal. III); it is frequently altered to bayldonite. Mottramite is abundant as compact or cellular masses with sometimes a reniform (IV) or botryoidal (V) surface. It is dark olive-green, with a pale yellow streak, and is readily soluble in hot dilute hydrochloric acid with evolution of chlorine. Full details of the method of analysis are given; the results agree with $4(Cu,Pb)O,V_2O_5,2H_2O$, in which $Cu:Pb=1:1$. Cuprodescloizite as crusts of small, dark olive-green crystals showing pyramidal points gave VI, corresponding with $4(Cu,Pb)O,V_2O_5,H_2O$, in which $PbO:(CuO+ZnO)=1:1$. A new lead copper arsenate, named *duftite*, forms pale olive-green crusts of small, indistinct crystals (resembling olivenite in form) on crystals of azurite. It is soluble in hot dilute hydrochloric acid. Anal. VII corresponds with $2Pb_3(AsO_4)_2,Cu_3(AsO_4)_2,4Cu(OH)_2$. The mineral contains no trace of chlorine or phosphoric acid, and consequently it has probably not been derived from mimetite, although it is sometimes associated with remains of this.

	PbO.	CuO.	ZnO.	MnO.	V_2O_5.	As_2O_5.	SiO_2.	H_2O.	Total.	Sp. gr.
III.	67·31	trace	—	—	—	23·12	—	—	99·76*	6·98
IV.	54·70	18·75	0·19	trace	21·05	1·25	0·28	3·93	100·15	5·93
V.	53·33	19·50	0·16	trace	19·20	3·04	0·70	3·92	99·85	5·90
VI.	54·90	16·27	3·51	trace	21·69	1·36	0·07	2·33	100·13†	6·19
VII.	50·10	19·32	0·46	—	—	26·01	0·44	2·73	99·81‡	6·19

* Incl. $PbCl_2$ 9·33 (Cl 1·38). † Also Fe_2O_3 trace. ‡ Incl. CaO 0·75

L. J. S.

Phosphate-bearing Pegmatites from Bavaria. H. Laubmann and H. Steinmetz (*Zeitsch. Kryst. Min.*, 1920, **55**, 523—586).—Phosphate-bearing pegmatites, similar to those near Limoges in France and Branchville in Connecticut, are described from five localities in Bavaria. The anhydrous phosphate minerals, fluormanganapatite, triplite, triphylite, and triploidite, are present as original constituents of the pegmatite, and by their alteration by thermal waters they have given rise to a great variety of well-crystallised hydrated phosphate minerals. The latter include the iron (ferrous and ferric) phosphates, dufrenite, beraunite, strengite, phosphosiderite, cacoxenite, and vivianite; manganiferous phosphates containing also iron and alkaline earths, such as fairfieldite, phosphophyllite, phosphoferrite, xanthoxenite, and kreuzbergite; rarely manganese ferrous phosphates of the heterosite-purpurite series; simple manganese phosphates are here, however, absent. Analyses are given of the following: I, altered triplite from Plössberg; the fresh material contains P_2O_5, 34·13%. II, triplite from Pleystein. III, triplite from Hagendorf. IV, triphylite from Hagendorf. V, strengite as good violet-blue crystals ($a:b:c=$ 0·8663 : 1 : 0·9776) from Pleystein; formula $Fe_2O_3,P_2O_5,8H_2O$. VI, phosphosiderite as almond-blossom-red crystals ($a:b:c=$ 0·5456 : 1 : 0·8905) from Pleystein; formula $Fe_2O_3,P_2O_5,7H_2O$.

VII, *phosphophyllite*, a new species, forming colourless or pale blue, monoclinic crystals ($a \cdot b : c = 1{\cdot}0381 : 1 : 1{\cdot}7437$, $\beta = 89°32'$) with

	P_2O_5.	Fe_2O_3.	FeO.	MnO.	Li_2O.	F.	Insol.	H_2O.	Total.
I.	19·73	—	41·60	31·03	—	6·28	1·03	—	—
II.	33·14	—	33·51	25·42	—	6·77	0·46	—	—
III.	31·89	—	35·50	28·66	—	7·29	0·83	—	—
IV.	44·43	—	35·06	11·40	8·59	—	0·60	—	—
V.	38·24	43·40	—	—	—	—	—	18·89	100·53
VI.	37·71	44·38	—	—	—	—	—	17·31	99·40

perfect micaceous cleavage, D 3·081, from Hagendorf; formula $P_2O_5,2\frac{1}{2}R''O,\frac{1}{2}K_2O + \frac{2}{3}SO_4Al-OH + 3H_2O$ or

$$3R_3P_2O_8 + 2AlOH{\cdot}SO_4 + 9H_2O.$$

VIII, *phosphoferrite*, a new species, from Hagendorf, occurring as cloudy-white or greenish, crystalline masses with greasy lustre.

	P_2O_5.	SO_3.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.	Ign.	Insol.	Total.
VII.	25·85	9·17	6·12	13·55	5·12	12·04	8·50	13·17	3·66	98·09*
VIII.	35·10	0·75	0·61	40·35	5·30	6·20	0·55	4·67	1·94	—†

* Including BaO 0·91. † Also MnO 2·46, Na_2O 0·25, SiO_2 1·03.

D 3·156. Formula $H_3PO_4,3PO_4,4\frac{1}{2}R''$ or $H_6R_9''(PO_4)_8$. The primary apatite contains P_2O_5 42·61, MnO 4·93, and no chlorine, and is therefore described as *fluormanganapatite*. *Kreuzbergite*, a new species from the Kreuzberg at Pleystein, forms small, colourless to pale yellow, orthorhombic crystals ($a : b : c = 0{\cdot}3938 : 1 : 0{\cdot}5261$), D 2·139, and consists essentially of hydrated aluminium phosphate with some iron, calcium, and manganese. *Xanthoxenite*, a new species from Rabenstein, occurring as small, wax-yellow, monoclinic crystals, D 2·844, intimately associated with dufrenite and cacoxenite; it is a basic ferric phosphate (P_2O_5, 32·61; loss on ignition, 16·10%) with some manganese and calcium. L. J. S.

Pickeringite from Opálbánya, Hungary. VIKTOR ZSIVNY (*Zeitsch. Kryst. Min.*, 1920, **55**, 629—631).—Yellowish-white, fibrous material with silky lustre gave (also traces of MnO, Na_2O, NH_3, P_2O_5):

SO_3.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	FeO.	H_2O.	Total.
36·62	9·52	4·04	4·06	0·70	0·23	45·42	100·59

agreeing with the usual formula, $(Al,Fe)_2(Mg,Ca,Fe)(SO_4)_4,22H_2O$. Together with other sulphates, the mineral is of recent formation in the levels of the opal mines, having been formed by the decomposition of the small crystals of iron-pyrites present in the hypersthene-andesite matrix of the opal. L. J. S.

Minerals from Madagascar and the Urals. RENÉ CHARLES SABOT (*Thèse, Univ. Genève*, 1914, 1—138; from *Jahrb. Min.*, 1920, i, Ref. 138—142).—Crystallographic and optical determinations, usually with analyses, are given for a number of minerals. Most of the data have been previously published (Duparc, A., 1910, ii, 221; 1913, ii, 782; 1914, ii, 664, etc.), but the following

analyses appear to be new. I, Muscovite, plumose mica, from Ampatsakana, Madagascar. II, Spessartite crystals from Takovaya, Urals. Blue apatite, occurring with rubellite and felspar at Antsongombato, Madagascar, gave: P_2O_5, 40·09; CaO, 54·45; MnO, 1·80; Cl, 0·20; F [3·46]; D 3·2013.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I.	44·35	37·40	—	5·30	0·30	0·19
II.	35·12	20·40	2·06	6·78	33·16	2·10

	MgO.	K_2O.	H_2O.	Total.	Sp. gr.
I.	1·67	5·94	5·29	100·44*	2·8908
II.	0·15	—	—	99·77	4·1577

* Also TiO_2, Na_2O traces.

L. J. S.

Optical Characters of Epidote. M. GOLDSCHLAG (*Tsch. Min. Mitt.*, 1917, **34**, 23—60; from *Jahrb. Min.*, 1920, i, Ref. 135—137).—Optical determinations were made on clinozoisite and epidote from various localities, and the results correlated with the chemical composition (percentage of ferric iron reckoned as an iron-epidote molecule). The following new analysis, by KAROLINE LUDWIG, is given of epidote from Pfarrerb, Zöptau, Moravia:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
38·34	26·11	9·67	1·07	23·93	0·34	n.d.	99·46

L. J. S.

Andesine from Hohenstein, Kremsthal, Lower Austria. O. GROSSPIETSCH (*Sitzungsber. Akad. Wiss. Wien*, 1918, **127**, 439—447; from *Jahrb. Min.*, 1920, i, Ref. 132).—Analysis of crystals gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	Ign.	Total.	Sp. gr.
59·98	24·67	0·54	7·26	trace	7·36	0·09	99·90	2·67

corresponding with $Ab_{65}An_{35}$. The optical constants are given.

L. J. S.

Analytical Chemistry.

Qualitative Chemical Analysis. V. MACRI (*Boll. Chim. Farm.*, 1920, **59**, 385—389).—The author gives a scheme according to which the metals are detected approximately in the opposite order to that of the method commonly employed, one advantage of this procedure being that it allows of the use of fixed alkalis or their salts. [See *J. Soc. Chem. Ind.*, 1920, November.]

T. H. P.

The Analysis of Aqueous Solutions with the Aid of the Refractometer. MAX DE CRINIS (*Zeitsch. physiol. Chem.*, 1920, **110**, 254—265).—The refractive index of salt solutions which do not manifest the phenomenon of molecular attraction is in direct linear proportion to the percentage of the concentration of the salt in the solution. On establishing this relation between the refractive index and the concentration of a solution, it is possible to calculate the percentage of the concentration by means of the formula $y = (nDX\% - 1{\cdot}33320)/b$ ($nDX\%$ = refractive index of $X\%$ solution, b = refractive index of 1% solution of the same salt, $1{\cdot}33320$ = refractive index of distilled water). The refractive index of a mixture of equal parts of various salt solutions is equal to the sum of the refractive indices of the solutions which make it up. If by mixing these salts some substance is precipitated, the refractive index of the precipitated salt can be obtained by subtracting the refractive index of the remaining solution from the sum of the refractive indices of the component solutions. The ion content of the aqueous solution can therefore be calculated, as follows: $P = (nDRX\% - nDOX\%)/K$. P = percentage; $nDRX\%$ = refractive index of $X\%$-solution obtained by calculation; $nDOX\%$ = refractive index observed after precipitation; $K = nDR1\% - nDO1\%$ of a 1% solution. S. S. Z.

A Simple Method for Titrating Electrometrically to a Desired End-point in Acid-alkaline Reactions. P. E. KLOPSTEG (*Science*, 1920, **52**, 18—19).—The hydrogen electrode can be utilised to compare a known standard solution with one of unknown p_H value. From the curves of Sörensen (*Ergebn. Physiol.*, 1912, **12**, 393) or the formulæ of Clark and Lubs (A., 1916, ii, 44) is selected the solution with p_H value corresponding with the point to which it is desired to titrate. This solution is placed in connexion (by means of a bridge of potassium chloride solution) with the unknown, each being provided with a hydrogen electrode. The two electrodes are connected by a tapping key and high-resistance galvanometer. Titration to an end-point is effected by merely adding solution until, on tapping the key, no deflection is observed, showing equal hydrogen-ion concentrations in the two solutions. The accuracy is limited by that of the p_H value of the standard solution. CHEMICAL ABSTRACTS.

The H-ion Concentration of some Standard Solutions at Various Temperatures. L. E. WALBUM (*Biochem. Zeitsch.*, 1920, **107**, 219—228; *Compt. rend. Soc. Biol.*, 1920, **83**, 707—709).—The H-ion concentration of mixtures of glycine and sodium hydroxide, borate and hydrochloric acid, and borate and sodium hydroxide increases with increased temperature between 10° and 70°. The reverse is the case with a citrate and sodium hydroxide mixture. In the former three mixtures, the alteration is more marked in the alkaline mixtures, but diminishes with the diminution of the alkalinity of the mixtures. S. S. Z.

Use of Ethyl Ether in Iodometric Estimations. L. GERET (*Mitt. Lebensmittelunters. Hyg.*, **11**, 67—68; from *Chem. Zentr.*, 1920, iv, 354).—Commercial ethyl ether can liberate large quantities of iodine in consequence of the presence of peroxidised substances. Such ether should be dehydrated with calcium chloride and subjected to prolonged treatment with metallic sodium, or shaken with concentrated alkali thiosulphate, rapidly dried over calcium chloride, and distilled. H. W.

Extensive Employment of Arsenious Acid in Volumetric Analysis. R. NAMIAS (*Giorn. chim. ind. applicata*, 1920, **2**, 176).—A reply to de Bacho (this vol., ii, 188).

CHEMICAL ABSTRACTS.

Application of the Thermal Conductivity Method to the Analysis of Complex Mixtures of Gases. E. R. WEAVER and P. E. PALMER (*J. Ind. Eng. Chem.*, 1920, **12**, 894—899).—The thermal conductivity method can only be applied quantitatively when the probable identity and amounts of constituents likely to be present in a gaseous mixture are known. For estimation of a constituent by comparison with a standard gas, air is the most suitable standard for mixtures with low conductivity, and hydrogen for those with high conductivity. This is suitable for estimating hydrogen in air, the relative proportions of hydrogen and ammonia in gases for synthetic ammonia processes, and impurities in hydrogen. In other cases, such as the estimation of chlorine, hydrogen chloride, sulphur dioxide, acetylene, and water vapour in various gaseous mixtures, the results are calculated by comparing the conductivities before and after a chemical reaction. Thus, the total amount of atmospheric gases in a hydrogen-filled balloon may be estimated by applying the method before and after the reaction of the oxygen with the hydrogen. Similarly, methane in air may be estimated by the difference in the results obtained before and after passing the air over hot copper oxide. Another modification is to add a gas to a mixture prior to the reaction. For example, in estimating oxygen in flue gas, hydrogen is first added, and the oxygen removed by combustion. The difference in the conductivities of the residual excess of hydrogen and nitrogen in the mixture is too small to affect the accuracy of the results for oxygen. In like manner, successive combustions with oxygen and hydrogen may be used for certain mixtures, as, for example, in estimating carbon monoxide in the presence of large amounts of hydrogen. C. A. M.

Estimation of Chlorine in Blood. M. RODILLON (*Presse méd.*, **28**, 85—86; from *Chem. Zentr.*, 1920, iv, 315—316).—A solution of trichloroacetic acid (1 : 5; 15 c.c.) is added slowly and with stirring to an equal volume of the well-centrifuged serum, and the mixture is passed through a folded filter. 11·7 c.c. of the filtrate (a portion is reserved for the estimation of carbamide) are treated with $N/10$-silver solution (10 c.c.), distilled water

(50—60 c.c.), and finally with ferric alum solution (10 c.c.); the mixture is thoroughly agitated and titrated with $N/10$-ammonium thiocyanate solution until the red coloration persists. H. W.

A New Method for the Estimation of Bromine. G. HARTWICH (*Biochem. Zeitsch.*, 1920, **107**, 202—206).—The urine is incinerated with sodium carbonate and acidified with sulphuric acid. Chlorine water is added and the liberated bromine is extracted with chloroform. The bromine is calculated from the quantity of chlorine used up. 347 Mg. of sodium bromide were estimated by this method in 100 c.c. of bromine-free urine with an error of about 3%. S. S. Z.

Use of Barcroft's Differential Apparatus. R. WERTHEIMER (*Biochem. Zeitsch.*, 1920, **106**, 1—11).—Replacement of Barcroft's formula (A., 1908, ii, 319, 529) by that of Münzer and Neumann (A., 1917, i, 520) gives for the gas volume a value higher by about 0·5%, or, if the barometric pressure is corrected for the pressure of the water vapour, lower by about 0·4%. Use of Barcroft's formula and neglect of the water-vapour pressure correction is hence recommended. Determination of the constants of the apparatus is described. T. H. P.

Investigations on Alveolar Gas Pressures by a New Method. PIUS SUPERSAXO (*Biochem. Zeitsch.*, 1920, **106**, 56—82). —The author has tested a new method, devised by Asher, for investigating alveolar air which permits of the estimation of both the carbon dioxide and the oxygen. The analysis is carried out by means of the Bunte burette, and as it requires 100 c.c. of air, Haldane and Priestley's method (A., 1905, ii, 400) is modified so as to yield increased quantities of the alveolar air. The method is fully described. T. H. P.

Estimation of Neutral Sulphur in Urine. PAUL LIEBESNY (*Biochem. Zeitsch.*, 1920, **105**, 43—48).—Estimation of the sulphur in sulphosalicylic acid solution by precipitation as benzidine sulphate was found to yield results 8—10% in excess of the true value, owing to the presence of sulphur compounds in the gas employed as source of heat during the operations. The author has therefore modified Raiziss and Dubin's method of estimating the total sulphur in urine (A., 1914, ii, 671), use being made of an electric combustion furnace. The total sulphates in urine may be estimated by Rosenheim and Drummond's method (A., 1914, ii, 485), the difference between total sulphur and total sulphates representing neutral sulphur. T. H. P.

Volumetric Method for the Estimation of Acids and Bases which yield Insoluble Salts. HANS TH. BUCHERER (*Zeitsch. anal. Chem.*, 1920, **59**, 297—302).—For the estimation of sulphuric acid, the hot solution containing the latter is titrated with N-barium chloride until the precipitation of barium

sulphate appears to be complete. A small portion of the solution is then filtered, and the filtrate divided into two portions, which are tested with a drop of barium chloride solution and a drop of dilute sulphuric acid respectively. If a precipitate is obtained with barium chloride, the titration is continued, and the solution again tested after filtration. In this way, the amount of barium chloride necessary for the precipitation of the sulphuric acid is ascertained approximately. The titration is then repeated on a fresh portion of the original solution, the final titration being made with $N/10$-barium chloride solution. Similar methods of titration may be used for the estimation of calcium (as oxalate), magnesium (as ammonium magnesium phosphate), etc.

W. P. S.

A Little-known Still-head for Kjeldahl Distillation. A. Prange (*Chem. Zeit.*, 1920, **44**, 681).—To guard against frothing over during distillation of ammonia when estimating nitrogen by the Kjeldahl process, the glass tube leading from the distillation flask to the receiver is inclined in an upward direction for some distance from the safety bulb. This gives additional security should the bulb become filled with froth. E. H. R.

The Technique for the Estimation of the Residual Nitrogen in Blood. Joh. Feigl (*Biochem. Zeitsch.*, 1919, **101**, 62—73).—A theoretical paper. Folin and Wu's method (A., 1919, ii, 308) is considered an improvement on other methods.

S. S. Z.

Colorimetric Estimation of Ammonia, Nitrites, and Nitrates. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 1253—1264).—In addition to the difficulty that colorimetric determinations are not accurate to within 5 to 10%, irregularities occur in practice from the influence of such factors as the quantity of reagent, the temperature, the time, the presence of retarding substances, etc. In the quantitative estimation of traces of ammonia by means of Winkler's reagent, which will detect 0·1 mg. NH_4 per litre, time was not found of great importance, the colour being at its maximum for different concentrations of the reagents after fifteen minutes in all cases. The quantity of reagent used has a marked effect, 0·3 c.c. of Winkler's reagent producing the same colour with 50 c.c. of a solution containing 0·6 mg. NH_4 per litre as 0·5 c.c. produced with the same volume of a solution containing 0·4 mg. NH_4 per litre. The strongest colour was obtained by adding 0·5 c.c. of the reagent to 50 c.c. of the ammoniacal solution. The presence of excess of potassium iodide depresses the sensitiveness enormously; the presence of 0·3 c.c. N-KI with 1 c.c. of the reagent and 50 c.c. of a solution containing 10 mg. NH_4 per litre reduced the colour to equality with that given by 50 c.c. of a solution containing 0·35 mg. NH_4 with 1 c.c. of the reagent, whilst 0·6 c.c. N-KI prevented the formation of the colour completely. The influence of a small excess of potassium

iodide varies with the concentration of the reagents. Bromides and thiocyanates have a preventive effect, although not so great as iodides. Chlorides have very little effect unless in large quantity. Sulphates have little effect on the colour, but hasten the separation of the orange precipitate. Secondary phosphates weaken the colour, whilst addition of excess of alkali hydroxide inhibits it entirely, as also does cyanide. A very satisfactory reagent, capable of detecting 0·1 mg. NH_4 per litre, is mercury sodium chloride in weak alkaline solution, which gives a white opalescence permitting of nephelometric estimation.

The recent work of Frederick (A., 1919, ii, 371) and Massink (*Water*, **3**, 89) on the phenol-sulphuric acid method of estimating nitrates is examined, and the influence of traces of chlorides shown by Massink to be necessary is confirmed, although the quantitative effect is greater than Massink stated. The test is best carried out by adding to the working solution 0·5 c.c. *N*-NaCl, evaporating to dryness, adding to the residue 2 c.c. of phenol-sulphuric acid, and warming for twenty minutes on the water-bath. The liquid is then diluted and rendered ammoniacal according to the procedure of Frederick. In the new form, the reaction is quantitative, the colour being proportional to the amount of nitrate present. Nitrites have very little effect on the reaction in this form. The brucine-sulphuric acid method was also examined, but no quantitative results could be obtained.

The Griess-Romijn method for the colorimetric determination of nitrite is also examined, and modifications are recommended. If 100 c.c. of the reagent be added to 50 c.c. of the solution under test, and the mixture warmed to 55—60° for five minutes, the maximum colour is reached at once on cooling. Since alkalis inhibit strongly, a hard water should first be made acid with acetic acid.

S. I. L.

Estimation of Ammonia in Urine, in Serous Liquids, and in the Oxidised Liquid of the Kjeldahl Method. ARNOLD HAHN and ELISABETH KOOTZ (*Biochem. Zeitsch.*, 1920, **105**, 220—228).—Using Hahn's modification of the Krüger, Reich, and Schittenhelm method, all the ammonia is expelled in five minutes from a solution containing 0·04 gram of ammonia as ammonium sulphate, 25 c.c. of water, 10 grams of sodium chloride, 1 gram of sodium carbonate, and 30 c.c. of 96% alcohol if the distillation flask is heated in a boiling-water bath and the distillation is carried out in the maximum vacuum given by a water pump. Under these conditions, carbamide (2 grams) yields no ammonia. Cooling of the receiver containing the standard acid for absorbing the ammonia is found to be unnecessary. Methods based on the above results are given for the estimation of ammonia in urine either free from, or containing, protein, in blood serum, and in the decolorised acid liquid of the Kjeldahl method. A special indicator containing sodium alizarinsulphonate and methylene-blue is used for titrating the alcoholic *N*/100-acid used in the case of blood serum.

T. H. P.

The Conductometric Titration of Phosphoric Acid and its Salts. I. M. Kolthoff (*Zeitsch. anorg. Chem.*, 1920, **112**, 165—171).—Phosphoric acid behaves as a strong acid, and cannot be titrated conductometrically in concentrated solution (compare this vol., ii, 420). In dilute solution it can be titrated in exactly the same way as a mono- or di-basic acid, the first equivalent point being very sharp, the second less distinct. The conductometric method of titration has the advantage over the indicator method that indicators give indistinct end-points in very dilute solutions of phosphoric acid. Secondary phosphates, for example, Na_2HPO_4, can be titrated with acids when the concentration is less than 0·01 molar. When the concentration is greater, the break in the conductivity curve at the point corresponding with primary phosphate is indistinct, owing to the dissociation of phosphoric acid. Secondary phosphates cannot be titrated with alkali, on account of the hydrolysis of the tertiary phosphates. Dilute solutions of pyrophosphates can be satisfactorily titrated with acid to the secondary salt. The break corresponding with the tertiary salt is indistinct. E. H. R.

Estimation of Carbon Dioxide in Alkali Hydrogen Carbonates in the Presence of Carbonates. Wilhelm Hartmann (*Zeitsch. anal. Chem.*, 1920, **59**, 289—297).—When a mixture of sodium hydrogen carbonate and sodium carbonate is mixed with 70% glycerol solution (7 c.c. for each 0·1 gram of carbonate) and heated at 115° for ten minutes, the whole of the carbon dioxide in the hydrogen carbonate is liberated, and, after being passed through suitable drying apparatus, may be collected in an ordinary potash bulb and weighed. At the end of the ten minutes the temperature should be lowered to 100°, and a current of air passed through the apparatus to convey the carbon dioxide into the potash bulb. If the same mixture is then heated at 190° for five minutes, two drops of water now added, and the heating continued for a further ten minutes, the carbonate is decomposed, and the resulting carbon dioxide may be collected and weighed. In most cases, the greater part of the water evolved with the carbon dioxide may be separated by means of a short reflux apparatus, but when ammonium salts are present, a vessel containing sulphuric acid must be used for drying the gas and removing the ammonia. W. P. S.

The Conductometric Estimation of Carbonic Acid and its Salts. I. M. Kolthoff (*Zeitsch. anorg. Chem.*, 1920, **112**, 155—164).—Solutions of carbonic acid, from 0·0015 to 0·02 mol. in strength, can be titrated conductometrically with alkali. The conductivity straight-line curve becomes steeper after the formation of the hydrogen carbonate, and again steeper after the formation of the normal carbonate. The breaks in the curve, however, are not sharp, especially in very dilute solutions, in which, owing to the considerable hydrolysis of the carbonate, the

straight-line portions become rounded into a continuous curve. The sharpness of the titration can be greatly increased by having present an excess of calcium salt (calcium chloride) to precipitate the carbonate as it is formed. Time must be allowed during the titration for the precipitation of the calcium carbonate.

Carbonic acid cannot be titrated with carbonate to the hydrogen carbonate conductometrically, because the angle between the two portions of the curve is too obtuse. On the other hand, carbonate can be titrated with acid. According to the dilution, the conductivity may fall (in dilute solution) or rise (in stronger solutions, above $0 \cdot 1N$) up to the hydrogen carbonate point. From this point, which is not sharp, to the neutral point, the conductivity increases gradually, and at the neutral point there is a sharp rise. The neutral point is very sharp in extremely dilute solutions. Free alkali hydroxide can be estimated in presence of carbonate by titration with acid if not present in too small an amount. The amount of hydrogen carbonate in carbonate can be determined by titration with alkali or acid, but its amount must not be too small, or the direction of the corresponding portion of the curve cannot be determined with sufficient accuracy. A very weak acid, such as boric acid, can be titrated in presence of sodium carbonate with alkali hydroxide with satisfactory results. E. H. R.

Microchemical Reactions of Radium; its Differentiation from Barium by Iodic Acid. G. Denigès (*Compt. rend.*, 1920, **171**, 633—635).—Radium salts give results identical with those of barium salts in the microchemical tests where hydrofluosilicic acid, oxalic acid, tartaric acid, potassium ferrocyanide, potassium tartrate, ammonium cyanurate, or ammonium phosphomolybdate in ammoniacal solution are used respectively as reagents. Iodic acid can be used, however, under certain conditions to differentiate between the salts of these two metals. If the concentration of the solution does not exceed 0·3%, radium and barium salts give typical and distinct microcrystalline precipitates with a 10% solution of iodic acid. W. G.

Titrations with Surface-active Substances as Indicators. II. Estimation of Acidity with Capillary-active Substances of Alkaline Nature. Wilhelm Windisch and Walther Dietrich (*Biochem. Zeitsch.*, 1919, **100**, 130—147. Compare this vol., ii, 48).—Salts of substances of an alkaline nature, such as quinine hydrochloride, veratrine hydrochloride, eucupine dihydrochloride, were used as indicators in acidimetric titrations, according to Traube's method, by changing the surface tension of the indicator. Eucupine dihydrochloride was found to be as sensitive as decoic acid is in alkalimetry. With this indicator, it is possible to carry out graduated titrations of a strongly dissociated acid in the presence of a primary phosphate in varying proportions. By this method, the amphoteric reaction of mixtures of primary and secondary phosphates can also be demonstrated. S. S. Z.

Titrations with Surface-active Substances as Indicators. III. Investigation of Carbonates and Phosphate–Carbonate Mixtures by Utilising Surface-active Indicators of Acid and Alkaline Nature. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **101**, 82—109. Compare this vol., ii, 48, and preceding abstract).—The carbonates and hydrogen carbonates of potassium and sodium react alkaline with eucupine dihydrochloride as a surface tension indicator; those of magnesium react less alkaline than the above, but more alkaline than calcium normal and hydrogen carbonates. When these carbonates are mixed with primary potassium phosphate in the cold, the two substances react until a certain equilibrium is attained, showing the same order of alkalinity as the above. This is obtained with the alkaline surface tension indicator, eucupine dihydrochloride, as well as with the acid surface tension indicator, sodium undecoate. When heated, the alkali carbonates have the same influence on the primary phosphate as alkali hydroxide. The action of magnesium and calcium hydrogen carbonates on the primary phosphate under these conditions is complicated. The alkaline action of the alkaline earth hydrogen carbonates is proportionately greater when small quantities are used than when larger ones are employed.

S. S. Z.

Estimation of Potassium as Perchlorate, and the Separation from Sodium, etc. R. LEITCH MORRIS (*Analyst*, 1920, **45**, 349—368).—A critical examination of the perchlorate method for the estimation of potassium, together with suggestions as to the most suitable forms of apparatus. The potassium salt solution should be evaporated three times with perchloric acid, and in the final evaporation taken practically to dryness. The residue is treated with 10 c.c. of wash liquid (100 c.c. of 98% by vol. alcohol and 1 c.c. of 20% perchloric acid), stirred occasionally for fifteen minutes when sodium is present, and the liquid then decanted through a weighed Gooch crucible containing asbestos. When only potassium is present, the precipitate is rinsed directly on to the filter with a small, measured quantity of the wash liquid. If sodium is present, the basin containing the precipitate from the first decantation is heated slightly to evaporate the alcohol, the precipitate dissolved in a small quantity of water, the solution evaporated to dryness, the precipitate treated with 10 c.c. of wash liquid, the latter decanted on to the filter, and the precipitate transferred by using 10 c.c. of the filtrate. Finally, the precipitate is washed on the filter by a measured volume of wash liquid, the crucible and its contents dried at 130° to 150° for one hour, cooled in a desiccator for one hour, and weighed. The weight is taken as being constant when, on washing with 3 c.c. of liquid, the difference between successive weighings does not exceed 0·2 mg. When much phosphoric acid is present, the evaporation with perchloric acid should not be to dryness, but to a moist, pasty condition; the residue is then treated with 15 c.c. of 98% alcohol, and finally washed with the wash liquid. Calcium, iron,

aluminium, and barium do not interfere, and magnesium is also without effect provided that the evaporation with perchloric acid is not carried to dryness. Organic acids tend to char during the evaporation, and when they are present it would seem preferable to separate the potassium previously by the cobaltinitrite method. In the case of sulphates, the sulphuric acid should be removed by treatment with barium chloride, but it is not necessary to remove the slight excess of barium chloride used. W. P. S.

The Precipitation of the Calcium Group and Magnesium. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1229—1234).—The sensitiveness of ammonium carbonate, as usually used for the precipitation of Group IV in presence of ammonium chloride, leaves much to be desired. Ammonium carbonate in the cold gives no precipitate with solutions containing less than 25 mg. of calcium per litre, and at that concentration the precipitate is visible only after fifteen minutes. The sensitiveness is greater at the boiling point; in presence of free ammonia, a concentration of 5 mg. of calcium per litre, shows a precipitate in boiling ammoniacal solution. Ammonium chloride renders the reaction much less sensitive. The same conclusions are found to hold for strontium and barium, the latter being least sensitive to ammonium carbonate, as would be expected from the solubilities of the Group IV metal carbonates.

Sodium carbonate is found to be a much more sensitive reagent, giving precipitates at the boiling point from solutions containing only 1 mg. of calcium, 3 mg. of strontium, or 5 mg. of barium per litre. The use of sodium hydroxide and carbonate together i recommended to ensure complete precipitation of magnesium, whic can be removed by the chromate method and reprecipitated wit ammonium phosphate. Considerable excess of these reagents i not harmful to the reaction, as the ammonia set free from th ammonium chloride present has no tendency to preven precipitation of the magnesium. S. I. L.

Estimation of Calcium and Magnesium in Differen Saline Solutions. E. CANALS (*Compt. rend.*, 1920, 171 516—518).—If to a solution containing calcium, magnesium, iron and aluminium salts, just acidified with sulphuric acid, sodiun phosphate is added and the solution made alkaline with ammoniun hydroxide, it is possible to retain the whole of the calcium and magnesium in solution by acidifying with acetic acid and shaking vigorously for several minutes. W. G.

Detection of Magnesium. FRITZ EISENLOHR (*Ber.*, 1920, 53 [*B*], 1476—1477).—Five c.c. of a solution of alkannin in alcoho (96%) are treated with a drop of $2N$-ammonium carbonate solution which does not cause any change in colour, and then with a drop of the neutral salt solution; the presence of magnesium, strontium, or manganese is denoted by the development of a bluish-violet coloration which becomes pale red after acidification with one or at most two drops of $2N$-hydrochloric acid; subsequent addition of the

same number of drops of $2N$-ammonium carbonate solution restores the bluish-violet colour only if magnesium is present. If the latter is present as magnesium ammonium phosphate, the salt is dissolved in $2N$-hydrochloric acid, and a drop of this solution is added to the alkannin tincture; further addition of 1—2 drops of ammonium carbonate causes the appearance of the bluish-violet colour if magnesium is actually present, whilst otherwise the original colour of the tincture is restored. It is essential that the alcoholic solution should not become diluted with water, since in this case the ammonia hydrolytically produced gives a blue coloration. H. W.

The Acidimetric Estimation of Heavy Metals in their Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 172—186).—Experiments were made to determine with what degree of accuracy the salts of heavy metals which form insoluble hydroxides can be titrated with alkali hydroxides, either by the conductometric method or with the help of indicators. The statement of Harned (A., 1917, ii, 272) that magnesium sulphate can be estimated conductometrically by titration with barium hydroxide was confirmed. Satisfactory results were also obtained by precipitating the magnesium hydroxide with excess of standard alkali, filtering, and titrating back with standard acid. The conductometric method gave unsatisfactory results when zinc sulphate was titrated with sodium or barium hydroxide, owing to the precipitation of basic salt. Better results were obtained by titrating sodium hydroxide with zinc sulphate. In the case of copper sulphate also, the formation of basic salt interferes with the titration, and satisfactory results could not be obtained. Mercuric chloride can be titrated conductometrically with accuracy by running the solution into sodium hydroxide solution, which should not be stronger than $0 \cdot 01N$. In the case of aluminium salts, when these are titrated with sodium or barium hydroxide, a sharp break in the conductivity curve is not obtained at the neutral point, but there is a very sharp break at the point where the formation of aluminate is complete. Aluminium hydroxide behaves, therefore, as a mono-basic acid. Aluminium sulphate or alum can be titrated with sodium hydroxide at the boiling temperature in presence of excess of barium nitrate, using phenolphthalein as indicator. Slight excess of alkali is run in and titrated back with acid. The results are accurate.

E. H. R.

Use of Diphenyl Derivatives in Qualitative Analysis. F. FEIGL (*Chem. Zeit.*, 1920, **44**, 689—690).—Benzidine and other diphenyl derivatives yield intense blue colorations with manganic, ceric, cobaltic, and thallic compounds. For the detection of traces of the latter their solution is rendered alkaline with sodium hydroxide solution prepared with ordinary tap water (the presence of calcium carbonate is advantageous since it occludes the traces of metallic hydroxides), the mixture filtered, and the filter then treated with a drop of benzidine acetate solution. The test will detect the presence of 1 part of manganese in 125 million parts of

solution. Thallic compounds even give a blue coloration with the reagent without previous treatment with alkali; cobalt salts must be heated with alkali solution to obtain the pink hydroxide before the reaction with benzidine can be obtained. In the case of iron the blue coloration is not obtained when all the iron has been precipitated from solution by alkali. W. P. S.

Electro-analytical Separation of Nickel (Cobalt) from Arsenic. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1789—1793).—Nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by the electric current. Cobalt on deposition carries down arsenic, whereas the nickel precipitate is free from arsenic. If the two metals are deposited simultaneously, arsenic may or may not be deposited, according to the conditions. J. R. P.

Volumetric Methods for Estimating Tin. J. G. F. DRUCE (*Chem. News*, 1920, **121**, 173—175).—Stannous tin may be more accurately estimated by a volumetric method in an acid solution. Titration with standard iodine solution in the presence of hydrochloric acid gives satisfactory results with stannous chloride, inorganic stannochlorides, and stannochlorides of aliphatic amines, but is less suitable for aromatic amine compounds, which have a tendency to darken during the titration, and so obscure the end-point. For the titration of stannous chloride with potassium permanganate solution, the hydrochloric acid should be kept as low as possible by dissolving the salt in dilute sulphuric acid, and titrating the solution as rapidly as possible. Potassium dichromate is usually less trustworthy as a reagent for the titration. C. A. M.

Estimation of Zirconium. MELVIN S. SMITH and C. JAMES (*J. Amer. Chem. Soc.*, 1920, **42**, 1764—1770).—Zirconium is precipitated by selenious acid from a boiling solution acidified with hydrochloric acid. The basic selenite on ignition leaves zirconia. It is shown that this method gives satisfactory results in the estimation of zirconium in a pure salt, in the separation of zirconium from aluminium and rare earths, and from iron when the amount of ferric oxide in the combined oxides of iron and zirconium does not exceed 10%. Titanium is precipitated with zirconium, and a correction must be applied in this case or the precipitation carried out in presence of excess of hydrogen peroxide, when zirconium alone is precipitated. If phosphates are present the zirconium phosphate in the ammonia precipitate is insoluble in hydrochloric acid, and must be fused with sodium carbonate, boiled with water, and the residue dissolved in hydrochloric acid and added to the main solution. A method for the analysis of zirconia ore is described. J. R. P.

Estimation of Antimony in Lead-Antimony Alloys. L. BERTIAUX (*Ann. Chim. anal.*, 1920, [ii], **2**, 273—278; *Bull. Soc. chim.*, 1920, [iv], **27**, 769—771; *Chim. et Ind.*, 1920, **4**, 467—472). —The alloy is dissolved by heating with sulphuric acid and

sodium sulphate, the solution is diluted with water, hydrochloric acid, and a few drops of a 0·1% solution of Poirrier's orange, and the mixture is titrated with standardised permanganate solution until the colour is just discharged. The hydrochloric acid keeps the antimony sulphate in solution, and as soon as all the antimony has been oxidised by the permanganate the next drop of permanganate solution introduced reacts with the hydrochloric acid, liberating chlorine, which decolorises the Poirrier's orange. Bismuth, copper, tin, and arsenic do not interfere; iron is titrated together with the antimony, but its quantity may be estimated colorimetrically with thiocyanate in the solution in which the antimony has been titrated. [See, further, *J. Soc. Chem. Ind.*, 1920, 693A.] W. P. S.

Sensitive Modification of Lieben's Reaction for Iodoform. RUDOLF KUNZ (*Zeitsch. anal. Chem.*, 1920, **59**, 302—303).—For the detection of traces of alcohol by this test, 10 c.c. of the solution are treated with 2 c.c. of 10% sodium hydroxide solution, 0·15 gram of potassium iodide and 0·2 gram of potassium persulphate, and the mixture is heated at 60°. A solution containing one drop of alcohol in 100 c.c. of water yields a turbidity, due to the formation of iodoform, within ten minutes. W. P. S.

The Conductometric Titration of Phenols. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 187—195).—Phenol and the cresols can be accurately titrated conductometrically with alkali in 0·1 or 0·01*N*-solution. Vanillin and sodium phenolsulphonate can be similarly titrated. In salicylic acid the hydroxyl group loses its acidic character and cannot be titrated, but its esters, for example, salol or methyl salicylate, can be accurately titrated as phenols; *p*-hydroxybenzoic acid behaves as a dibasic acid. Thymol and β-naphthol are also satisfactorily titrated. Of the dihydroxybenzenes, catechol behaves as a monobasic acid, the conductivity curve showing only one break, corresponding with the first hydroxyl group; quinol behaves as a dibasic acid, the first break not being very distinct, whilst resorcinol, which also behaves as a dibasic acid, gives better results when titrated with barium instead of sodium hydroxide. Pyrogallol functions as a dibasic acid, not monobasic, as stated by Thiel and Roemer (A., 1908, i, 787, 791), and so does phloroglucinol, whilst gallic acid, having a carboxyl in addition to three hydroxyl groups, behaves as a tribasic acid.

E. H. R.

Estimation of Terpin. OBDULIO FERNÁNDEZ and N. LUENGO (*Anal. Fis. Quim.*, 1920, **18**, 158—165).—When terpin is treated with acetic anhydride and anhydrous sodium acetate, only one of its two hydroxyl groups is acetylated; hence it behaves like a monohydric alcohol, although the results are slightly high. When a small quantity of sulphuric acid is used instead of sodium acetate, the reaction takes place spontaneously, and one hydroxyl group is acetylated. The quantity of acetic anhydride required is two to three times that of the terpin, the mixture being left for

one or two hours. Complete esterification is achieved by Boulez's method (A., 1907, ii, 306): 5 grams of terpin are dissolved in 25 grams of rectified oil of turpentine and 40 grams of acetic anhydride. Three grams of fused sodium acetate are added, and the mixture boiled for three hours. The liquid is digested for twenty minutes on the water-bath with a little water, and a saturated salt solution added; the top layer is made up to 100 c.c. with oil of turpentine and dehydrated with calcined sodium sulphate; an aliquot part of the liquid is then hydrolysed with alcoholic $N/2$-sodium hydroxide solution. W. R. S.

An Accelerated Method of Estimating the Reducing Values of Cellulosic Substances. E. KNECHT and L. THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 255—257).—Schwalbe's method for estimating the copper number of oxycellulose is modified by adding the cuprous oxide to a ferric salt solution and titrating the ferrous salt so formed with potassium permanganate. By this means it is unnecessary to determine the unreduced copper absorbed by the cellulose (copper hydroxide number), which is the difference between the above number and that obtained from an estimation of the unreduced copper in the filtrate by titanous chloride.

The copper number may be determined by a process based on the fact that oxycellulose precipitates cuprous thiocyanate from solutions of the cupric salt. This method avoids the errors that the action of the alkali hydroxide in Fehling's solution on oxycellulose may cause.

The copper number may also be determined by heating oxycellulose with sodium hydroxide and rosinduline, and then titrating with titanous chloride to determine the amount of dye reduced.

All three methods give sufficiently accurate results, and are more quickly carried out than the original Schwalbe method. [See *J. Soc. Chem. Ind.*, 1920, 718A.] A. J. H.

Estimation of Acetic Anhydride. KNUT WOLGAST (*Svensk Kem. Tidskrift*, 1920, **32**, 110).—Twenty-five c.c. of acetic anhydride are dissolved in 30 c.c. of benzene, 25 c.c. of water are added, and after vigorously shaking for fifteen seconds the aqueous layer is drawn off and measured. The increase in volume is due to the acetic acid present, and multiplied by 4 gives the percentage of acetic acid. Some small amount of acetic anhydride will dissolve in water and some of the dilute acetic acid will dissolve in the benzene. A table of corrections is necessary In the following pairs of figures the first is the burette reading of increased volume multiplied by 4 and the second the corrected percentage: 93·5—100, 90—95·6, 85—89·6, 80—81·5, 75—75·8, 55—55·1, 50—50·1, 35—33·3, 25—21·7, 20—15·5, 11—0. CHEMICAL ABSTRACTS.

Colour Test for Oxalic Acid. LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 1784—1785).—A few crystals of resorcinol are dissolved in 5 c.c. of the solution by warming gently. The

liquid is cooled and an equal volume of concentrated sulphuric acid slowly poured in to form a layer. A blue ring is formed at the junction of the layers if oxalic acid is present. If the blue colour does not appear, the liquids are mixed by shaking, and, after cooling somewhat, another 5 c.c. of sulphuric acid added. If the colour still fails to appear, the liquid is warmed over a flame (not boiled), when an indigo-blue colour appears. If the mixture is boiled the colour becomes dark green. J. R. P.

Detection of Coumarin in Vanillin. L. Geret (*Mitt. Lebensm. Hyg.*, 1920, **11**, 69—71).—Five % of coumarin in vanillin can be detected by the yellow turbidity produced by the addition of a 1% solution of iodine in 2% potassium iodide solution; the turbidity changes to lustrous, metallic, bluish-black crystals containing 46·47% of iodine and yielding 13·36% of ash.

Chemical Abstracts.

Estimation of Aminoethyl Alcohol and of Choline appearing on the Hydrolysis of Phosphatides. P. A. Levene and T. Ingvaldsen (*J. Biol. Chem.*, 1920, **43**, 355—378).—The method is a modification of that introduced by Thierfelder and Schulze (A., 1916, i, 548). This method is employed in the original form up to the point where the free aminoethyl alcohol is extracted. This is accomplished by boiling the mixture of the hydrochlorides of the two bases and an excess of calcium oxide with dry acetone. The combined acetone extracts are acidified with hydrochloric acid, and evaporated in a vacuum. The residue is dissolved in water, evaporated to a syrup, and again treated with calcium hydroxide and acetone. The final acetone extracts are filtered, made acid with hydrochloric acid, and the acetone removed by vacuum evaporation.

The residue from the acetone extracts is treated with water and filtered from calcium hydroxide. Hydrochloric acid and the residual calcium are removed by silver oxide and carbon dioxide respectively. The choline is precipitated as picrate.

In an actual experiment on the separation of the bases from the ether-soluble, acetone-insoluble lipoids from egg, 77·5% of the amino-nitrogen was found present in the acetone extracts, whilst the yield of choline was 98·7% of the theory. J. C. D.

Separation and Estimation of Phenylalanine. Shintaro Kodama (*J. Tokyo Chem. Soc.*, 1920, **41**, 479—495).—In the ester or the lime method glutamic acid, aspartic acid, and phenylalanine are collected in the same fraction. The author adds lime to the mixture of the products of hydrolysis of a protein, whereby basic calcium glutamate is precipitated. The calcium salts subsequently obtained by concentrating the filtrate are washed with water or lime-water, heated with 7 to 8 volumes of water, and treated with carbon dioxide, whereby calcium carbonate is precipitated. When this filtrate is concentrated, phenylalanine crystallises.

An approximate estimation of the phenylalanine in a mixture of the calcium salts of phenylalanine (Ca, 9·98; H_2O, 8·91%), glutamic

acid (Ca, 16·80; H_2O, 22·56%), and aspartic acid (Ca, 16·51; H_2O, 29·63%) can be made if the percentage of calcium and of water of crystallisation is estimated. By suspending the mixture in hot water and treatment with carbon dioxide, calcium glutamate and aspartate lose one-half of their calcium, and are converted into easily soluble, normal calcium salts, whilst the calcium salt of phenylalanine loses the whole of its calcium, and is converted into the free acid. The difference between the amount of calcium in the precipitate and in the solution corresponds with the amount of calcium originally combined with phenylalanine.

Several methods of obtaining perfumes from phenylalanine are described. CHEMICAL ABSTRACTS.

Estimation of Taurine in Muscle. Y. OKUDA and KEIICHI SANADA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, **7**, 77—80).—Sulphur is estimated in an aqueous extract of the muscle, after removal of all compounds of sulphur except taurine, for example, proteins, sulphates, and cystine (if necessary). The flesh (5 grams if fresh, 1 gram if dry) is ground and extracted first with cold water, then with warm water. The total extract is boiled with the addition of acetic acid; the coagulum is removed; the filtrate is neutralised, and is precipitated with basic lead acetate, an excess of that reagent being avoided. The precipitate is removed by filtration; the filtrate is treated with sulphuric acid to precipitate the excess of lead; excess of sulphuric acid is removed with baryta, and excess of baryta with ammonium carbonate. The final filtrate is used for the estimation of sulphur, which is converted into sulphate and weighed as barium sulphate. Multiplication of the weight of barium sulphate by the factor 0·5358 gives the weight of taurine. Cystine is usually absent from the extract; if it is present, the above technique is modified; after precipitation of the excess of lead, more sulphuric acid is added until its concentration reaches 5%; the cystine is then precipitated with phosphotungstic acid and removed by filtration after remaining for two or three days. Treatment with baryta and with ammonium carbonate and estimation of taurine sulphur are made as usual. The percentage of taurine in fresh flesh and, in parentheses, in dry flesh, was: shark, 0·13 (0·61); carp, 0·13 (0·61); ordinary flesh of bonito, 0·08 (0·30); "chiai" flesh of bonito, 0·42 (1·56); *Neptunus pelagicus*, 0·28 (1·37); *Palinurus vulgaris*, 0·17 (0·76); *Pinna japonica* (adductor muscle), 0·54 (2·38); *Avicula martensii* (mantle), 0·91 (5·20). All the samples of muscle (fish, mollusc, and crustacean) examined contained taurine; that compound was most abundant in molluscs, and less abundant in fish, although present in comparatively large amount in their "chiai" flesh. CHEMICAL ABSTRACTS.

Detection of Cyanic Acid. R. FOSSE (*Compt. rend.*, 1920, **171**, 635—637).—The cyanic acid may be detected directly as such or after its conversion into silver cyanate. In the first case a portion of the solution is heated for one hour with ammonium chloride, and the carbamide present in 2 c.c. of the solution thus

reated and in 2 c.c. of the untreated solution is estimated by neans of xanthhydrol. An increase in the carbamide content of the olution by heating with ammonium chloride is evidence of the resence of cyanic acid. In the second case the silver cyanate is eated with ammonium chloride, and the resulting liquid tested for arbamide as above. Another portion of the silver cyanate is first eated with nitric acid and then with ammonium chloride, but in his case there is no formation of carbamide. W. G.

Volumetric Estimation of Thiocyanate by Potassium Permanganate. R. MEURICE (*Ann. Chim. anal.*, 1920, [ii], **2**, 72—273).—Trustworthy results are obtained when the thiocyanate olution is acidified with sulphuric acid, treated with an excess of tandardised potassium permanganate solution, and the excess of he latter then titrated with dilute hydrogen peroxide solution. The excess of permanganate added should be at least one-half of hat required for the oxidation of the thiocyanate. Direct titration f thiocyanate in acid solution with permanganate yields low esults. W. P. S.

Detection of Hydrogen Cyanide. JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 16. Compare P., 1910, **26**, 115).—Filter paper is moistened with a reagent consisting of *o*-tolidine gram, copper acetate 1·5 grams, glacial acetic acid 0·5 gram, nd water 100 c.c., and is then suspended in the atmosphere to e tested. A blue colour appears on the paper if the air contains s little as 1 part of hydrogen cyanide in 2 millions. W. P. S.

Preparation of Phosphomolybdic Acid and its Application to the Colorimetric Estimation of Uric Acid. . PROSCHOWSKY (*Kongl. Vet. Landbohöjskole Aarskrift*, 1918, 72—407; from *Chem. Zentr.*, 1920, iv, 315).—The author reviews e colorimetric methods which have been proposed for the estimaon of uric acid in urine, and indicates a new procedure for the reparation of phosphomolybdic acid required in Höst's process; has been examined in detail, and certain improvements ·nded. H. W.

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...sm. IX. Detection and Estimation of ...e Purines in Human Blood and Pus ... HAUSER and G. CZONICZER (*Zeitsch. physiol.* ...—320. Compare A., 1919, i, 228).—For the timation ... in blood the serum is diluted with ater and precipitated with 1· 55% uranium acetate. The filtrate boiled with some sodium acetate and sodium hydrogen sulphite nd precipitated with 10% copper sulphate. The precipitate is ntrifuged, washed, and the nitrogen in it is determined by the icro-Kjeldahl method. From the value obtained, the free purine ntent is calculated. The figures of the uric acid content of serum btained by the colorimetric method and by the above method gree fairly well, and it is therefore to be concluded that only very

small quantities of free purines other than uric acid are presen[t] in the blood. In order to estimate the combined purines (nucleotides) in the blood, the diluted serum is boiled, and precipitated with a 20% solution of sulphosalicylic acid in order to remove th[e] proteins. The filtrate is concentrated and the purines are precipitated with copper sulphate as previously described, and the total purines are obtained from the nitrogen estimation, whilst the combined purines are calculated by difference. One hundred c.c. of normal human serum contain 2—3 mg. of nucleotide nitrogen and 1—1·5 mg. of free purine nitrogen. S. S. Z.

Colorimetric Estimation of Adrenaline. WILBUR L. SCOVILL[E] (*J. Ind. Eng. Chem.*, 1920, **12**, 769—771).—A mixture of 20 c.c. of water, 5 c.c. of 1% potassium iodate solution, and 0·25 c.c. of N/1-hydrochloric acid is heated at 38°, and 0·5 c.c. of a 0·1% solution of the sample is added. A similar mixture is prepared but using 0·5 c.c. of pure adrenaline solution. Both mixtures ar[e] kept at 38° for fifteen minutes, then cooled, and the coloration compared. If the coloration of the test solution differs by mor[e] than 25% from that of the standard, the estimation should b[e] repeated, using more or less of the solution. The pure adrenalin[e] solution is prepared by dissolving 0·5 gram of the substance i[n] 0·5 c.c. of N/1-hydrochloric acid and diluting the solution t[o] 50 c.c.; if the solution to be examined contains sodium hydroge[n] sulphite, 0·05 gram of the latter should be added to the standar[d] solution. W. P. S.

Important Source of Error in the Examination of Urin[e] for Albumin with Sulphosalicylic Acid. GRETE LASCH an[d] JOSEF REITSTOETTER (*Münch. med. Woch.*, 1920, **67**, 484—485; from *Chem. Zentr.*, 1920, iv, 30).—Schall's assumption (this vol. ii, 398) that sulphosalicylic acid forms a precipitate with calciu[m] chloride which can be mistaken for a precipitation of albumin [is] untenable. H. W.

Detection of Slight Traces of Hæmoglobin i[n] Urin[e] rine in J. PITICARIU (*Compt. rend. Soc. Biol.*, 1920, **83**, 605– ·5 (0·61); *Chem. Zentr.*, 1920, iv, 31).—Spectroscopic ·3 (0·30); "chiai" fectly fresh urines which contain traces o[f] *gicus*, 0·28 (1·37); which Ehrlich's reagent (dimethylami[n] (adductor muscle). chloric acid) has been added, shows the c[haracteristic] ·1 (5·20). All the bands of oxyhæmoglobin at dilutions at ·ean) examined con not the case. ·ndant in moll

[**Quantitative Comparison of Vitamine** ... ·ent. WALTE[R] H. EDDY and HELEN C. STEVENSON (*J. Biol. Chem.*, 1920, 4[3], 295—309).—The methods proposed by Bachmann (A., 1919, i, 61[3]) and by Williams (A., 1919, i, 46) have been used for quantitati[ve] studies on the vitamine-*B*. A new technique is described whic[h] eliminates some of the difficulties in the manipulation of the two tests. It is shown that this method may be utilised [for] estimating the vitamine content of food. J. C. D